

PROCEEDINGS
OF
THE PHYSICAL SOCIETY
OF LONDON.

JANUARY 1881.

XII. *Air-Thermometers.* By D. WINSTANLEY*.

[Plate V.]

A THERMOMETER which makes its indications in consequence of the dilatation and contraction of a gas offers several advantages over one which depends therefore on the volumetric variations of a liquid. Gases under constant pressure expand considerably more than liquids do for the same elevation in their temperature. Hence an air- or gas-thermometer, having the same size of bulb and tube as one in which a liquid only is employed, will have a more legible and open scale. Again, a given volume of a gas at the ordinary barometric tension of the air upon the level of the sea, when compared with an equal volume of a liquid body, requires so utterly insignificant an amount of heat to elevate its temperature through a given range, that a gas-thermometer is enormously more sensitive than one which depends upon a liquid for its expansional effects. And, finally, the very equal manner in which gases are dilated under the influence of equal increments of heat is a very strong point in favour of an air-thermometer.

As constructed by Galileo, the air-thermometer unfortunately gave readings which were influenced by the barometric

* Read June 26th, 1880.

variations of the outer air, a circumstance which has limited considerably its use and application. Happily it is not difficult to construct an instrument which shall be free from this defect. If we take an ordinary mercurial barometer made after a certain well-known pattern, *i. e.* with a bulb-shaped cistern surmounted by a neck into which we may insert a cork, and if as a matter of fact we *do* insert a cork, obviously that barometer ceases to show the tension of the outer air, and is a barometer only to the air enclosed within its bulbous cistern. But as the tension of this air will vary with its temperature, the height of the mercurial column will vary therewith as well; and that which *was* a barometer will, by the mere insertion of a cork, have become an air-thermometer, the readings of which are uninfluenced by the barometric variations of the external air. There is, of course, no reason why the tube of such an instrument should be so little or so much as thirty odd inches long. Neither is it necessary that mercury should be the liquid used. Sulphuric acid, for instance, will answer just as well. It is not even needful that the liquid should be non-volatile at the temperatures to which the apparatus is exposed. The objection which exists to the employment of a volatile liquid in the ordinary barometric column does not here apply; for that depression which the vapour tends to produce in one limb it tends to produce in the other one as well, and so leaves the equilibrium of the liquid undisturbed, and dependent only on the expansion and contraction of the air. It is merely needful, then, in this form of air-thermometer, that the gas enclosed shall be submitted to the definite pressure of an isolated barometric column; and we may employ what liquid and what length of tube we please. We may even construct a veritable air-thermometer *without* a barometric column by resorting to some other means of obtaining the definite pressure we require; and to this end the author has employed a vacuous corrugated elastic box similar to those contained in aneroid barometers; but he has used it with the spring inside. This thermometer is shown in fig. 1. At the bottom we have a rigid box with the elastic one enclosed. The rigid one is sealed; and the elastic one is surrounded by a liquid which rises some distance up a tube, in which the indications will be made. The tube is sur-

mounted by a bulb of air. This air, with a rise of temperature, expands and forces down the substance of the liquid column into the space made for it by the compression of the elastic box; and with a fall of temperature the reverse of course takes place.

The air-thermometer which I first described (that with the isolated barometric column) cannot, in the shape in which I have described it, be regarded as having a convenient form, inasmuch as through the greater portion of its length the liquid will never move. Obviously the index of the barometric column will not reach the level of the liquid in the cistern until the rational zero is attained; and the amount of space which marks the range between the freezing- and the boiling-points of water will have nearly three times as large a space below, devoted for the greater part to readings which will very likely never be observed.

I find, however, a very convenient instrument may be produced if, in its construction, two liquids are employed, as shown in fig. 2. There we have a mercurial barometric column. Its cistern is connected with the bulb of air by a long and upright tube. A column of sulphuric acid rests upon the mercury within; and the summit of the barometric tube is considerably enlarged. The tube connecting the barometer-cistern with the bulb of air is comparatively narrow in its bore. In consequence of this arrangement, the vertical amount of liquid motion is practically confined to the substance of the lighter column, and is several times greater in extent than if one liquid only had been used. We are accordingly enabled in this way to make an air-thermometer, of which the index shall move over pretty nearly its total length for such natural changes in temperature as we meet with in a given place. Such an instrument was constructed for me in Paris in 1878. It has hung in the Loan Collection of scientific instruments at South Kensington Museum for something like a year; and the accuracy of its indications does not seem impaired. The desirability of using coloured sulphuric acid as the material of the lighter column will very likely be a matter for dispute. I am aware that other experimentalists who have employed it in barometers have found a depression of the column has ensued and a crystalline deposit been left on the mercurial

surface. It is for me, however, to speak as I have found. Twelve months ago my instrument, when laid down flat, had a bubble of air in the mercurial limb purposely introduced, and of obviously less volume than a small pin's head. The instrument has never been reversed to float it out, and the volume of this air is still capable of the same description as before. This thermometer is four feet or more in length; and the diameter of its index-column (which is cylindrical) is the tenth of an inch or so. Its Fahrenheit degrees are represented by spaces of the third part of an inch; and it attains an exceedingly close approximation to the actual temperature of the air in some few seconds' time; whilst an alcohol thermometer, moving an equal column through equal spaces for equal numbers of degrees, and with a bulb similar in shape but proportional in size, requires some hours to reach an equally close approximation to the temperature of the air.

The air-thermometers I have now described have depended for their indications on the movements of a liquid in a tube. I have, however, devised another, in which the movement of the tube about the liquid is the method I employ. In this thermometer (fig. 3) the barometric tube is circularly curved and mounted concentrically upon a wheel of brass, which is supported in a vertical position by a knife-edge of hardened steel which passes through its geometric centre and rests on agate planes. Adjustments are provided by means of which the centre of gravity of this arrangement can be raised or lowered; and the mercurial column which is seen extending on the right is balanced by a weight, which is seen depending on the left. The whole is surmounted by the bulb of air; and the vacant space above the mercury upon the right is the Torricellian vacuum of the barometric column. Changes in temperature are shown by this thermometer in the varying angular positions of a needle, prolonged from one or other of the radii of the wheel, and counterpoised by a piece of metal on the other side. When the centre of gravity of this system has been made coincident with the point on which it turns, the liquid, under changes of temperature, is almost absolutely motionless, whilst the tube which holds it moves. By bringing the extremity of the needle into contact with a cylinder driven by clockwork at an even speed, we have a thermograph

complete. Of course some delicate method of recording must be used; and I have hitherto employed the smoked-paper process, so much adopted in the observatories of France. I prefer to make my records on the albumenized paper prepared for photographic use, and, for the sake of the beauty of the black, to smoke it over the flame of a common tallow dip. I then fix the records by immersing, cylinder and all, in lac varnish diluted with methylated spirit. In this process there is not the slightest danger of injuring the results; and these, when several times revarnished and mounted upon card and rolled, are doubtless permanent, and are certainly incomparably more beautiful than any other tracings I have seen.

XIII. *On Action at a Distance.* By WALTER R. BROWNE, M.A., M. Inst. C. E., late Fellow of Trinity College, Cambridge.*

THE object of this paper is partly historical, partly critical. In discussing what is called "Action at a Distance," the statement is frequently made that Newton was of opinion that "nobody who possessed a competent faculty of thinking" could possibly imagine such a thing to exist. The writer wishes, first, to show historically that this is by no means an accurate representation of Newton's views, and, secondly, to consider critically whether the repudiation of "action at a distance," which is now certainly common, is, after all, justified by the facts of the universe.

In the first place, Newton's words, contained in the Third Letter to Bentley, are as follows:—"That gravity should be innate, inherent, and essential to matter, so that one body may act on another body at a distance through a vacuum, without the mediation of any thing else by and through which their action and force may be conveyed from one to the other, is to me so great an absurdity that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it. Gravity must be caused by an agent acting constantly according to fixed laws; but whether this agent be

* Read November 13, 1880.

material or immaterial I have left to the consideration of my readers."

Now, in speaking of this passage, it is usual to quote the first of these sentences only, and omit the second ; and yet it is obvious that the second is intended to explain and define the sense of the first. Read by the light of the second, it seems perfectly clear that all which is denied in the first is the possibility of gravity being an inherent property of matter, in the sense in which hardness, inertia, &c. may be considered as properties. What Newton might seem to have had in his mind was the coarse materialism of Democritus and Lucretius, which held that all the phenomena of the universe were due to the mere motions and clashings of its ponderable atoms. This at least, he would hold, was disproved by his discoveries, because to defend it by assuming an occult property of matter, which could extend to a distance, was absurd. All, however, which he really says is that one body cannot, *uncaused*, act on another at a distance. In the second sentence he expressly uses, not indeed the word Cause, but the much stronger word Agent ; and he distinctly contemplates the possibility of this agent being, not material, but immaterial. It seems clear, therefore, that he is thinking of nothing less than of denying that action at a distance may, as a matter of fact, exist. Indeed, when we consider that this passage occurs, not in a mathematical work, but in a letter expressly treating of the relation between the discoveries of science and the doctrines of theology, and when we remember the strong theological views which he is known to have held, it seems impossible to doubt that he would have been perfectly contented to acquiesce in the immaterial nature of the agent of gravity ; though, no doubt, he would have been perfectly open to consider any reasonable hypothesis of a material agent which might have been placed before him.

Having thus attempted to restore the true sense of this famous passage, the writer will go on to consider, in the second place, how far the conception of Action at a distance actually merits the condemnation it has received. It seems desirable to commence with a definition, and to lay down the consequences which flow from it in general, before proceeding to consider particular cases.

Definition.—"By the term 'Action at a distance' is meant that direct action takes place between two bodies, separated from each other by a finite distance, without the intervention of any other body whatever."

Now if action at a distance does not exist, then the only *direct* way in which one body (A) can act upon another (B) is by coming into absolute contact with it; and the only *indirect* ways in which it can act upon it are two, viz. either by projecting a third body from contact with itself into contact with B, or by diverting some third body which, if not diverted, would have come into contact with B.

If action at a distance does not exist, all the actions between all the bodies of the universe must be explicable, by impact, on one of these three hypotheses. If any phenomenon takes place which cannot be so explained, then action at a distance does exist. It may be added that, if it is shown to exist in any one instance and at any distance, there is no probability against its existence in any other instance and at any other distance. It is no less wonderful, and no more wonderful, that two bodies should act on each other across the hundred millionth of an inch, than that they should act on each other across a hundred million of miles. In fact it is easy to conceive a creature so large, or so small, that the difference between these two distances would appear to it quite insignificant.

Let us now take the above three hypotheses and see whether all the actions in the universe can be explained by them.

First, as to the direct impact of one interacting body A upon another B. This may no doubt explain certain obvious cases, as the stoppage of a falling body when it reaches the earth; but it is equally obvious that there are many others, such as gravity, magnetism, &c., which it cannot explain. In fact, it will be granted that in these and many other cases there is an *apparent* action between bodies at a distance; and our business is to see whether it is real or apparent only.

Secondly, with reference to the projection of other bodies from A against B. It is clear that the actions thus produced can be actions of *repulsion* only: therefore this principle cannot explain any case of attraction. Moreover the power by which A is able to project these bodies against B itself requires explanation. If they have previously been at rest in

relation to A, then A can only project them by some innate explosive power totally different from impact. And if any one suggests that the bodies have previously been in motion with respect to A, and that they are projected by elastic reaction from A, then he must be asked to give an explanation of elasticity from impact only, and without introducing action at a distance. In any case it seems clear that this principle will not carry us very far in explaining the actions of the universe.

Thirdly, we have the principle that A may stop certain other bodies, which would otherwise have impinged upon B. This principle, as is well known, was applied by Le Sage to explain the facts of gravitation*. His hypothesis was that showers of "extramundane particles" are sweeping through space equally in all directions, and that a fraction of these, being intercepted by A and B, urge those two bodies towards each other. This hypothesis is encumbered with a large number of arbitrary assumptions; and the latest supporter of the theory, Mr. S. Tolver Preston†, presents it under a greatly modified form. He supposes the solar system to be immersed in an impalpable gas, the particles of which have a mean length of free path greater than the distance through which gravity has been observed to hold (greater, therefore, than the distance between the Sun and Neptune), and which tend to bring together, by the resultant of their impacts upon them, any two bodies within that range. It is not proposed in this paper to attempt an exhaustive discussion of this theory; but were it left as an unquestioned explanation of gravitation, it might be thought a strong presumption that all other actions were to be explained on the same principle. It may therefore be remarked that it is encumbered by very serious difficulties. In addition to those put forward by Dr. Croll and others, the following may be suggested:—

(1) Mr. Tolver Preston founds his theory on the late Prof. Maxwell's proof‡, that "a self-acting adjustment goes on among a system of bodies or particles in free collision, such that the particles are caused to move equally in all directions,

* Sir W. Thomson, *Phil. Mag.* May 1873.

† *Phil. Mag.* Sept. 1877, Nov. 1877, Jan. 1878.

‡ S. Tolver Preston, *Phil. Mag.* Sept. 1877.

this being the condition requisite to produce equilibrium of pressure”*. Now this equilibrium of pressure, and the theory based upon it, may be perfectly true for all known gases. But all such gases are under certain conditions, which need not hold universally; in especial they are *bounded* in some way. The atmosphere, which is the freest gas we can observe directly, is bounded by the earth on one side and space on the other, and is prevented from passing into space by the action of gravity. But we have no right whatever to assume such a boundary for interstellar space, or to assume that a gas filling such a space would have equilibrium of pressure. The probability would seem to be the other way; for any disturbance in such a gas would tend to propagate itself in all directions for ever. In any case, Maxwell’s results must be proved, not assumed, to hold for this gravity-gas, as it may be termed.

(2) Another difficulty in the theory is the enormous degree of porosity which it postulates for solid bodies. To fix our ideas, suppose that, in any unit of surface of a solid, one millionth part only is occupied by the really solid part (*i. e.* the part which would stop the particles of the gravity-gas) of the molecules composing that surface. Then it is obvious that a layer of such molecules a few millions thick would be practically certain to stop the whole of the gravity-particles impinging upon it. No arrangement of the molecules one behind the other will get over this, because the gravity-particles are assumed to come in all directions at once. Now such a layer would certainly be no more than a small fraction of an inch in thickness. And yet it is absolutely necessary for the theory (in order to explain how gravity varies as mass) to suppose that these gravity-particles pass through the 16,000 miles of the earth’s diameter, under the enormous density, pressure, and temperature which must exist in the interior, without having more than a very small proportion of their number stopped in the passage. The difficulty is rendered the greater when we remember that, *ex hyp.*, these attenuated molecules cannot act on each other at a distance, in producing the various

* I have, unfortunately, failed to verify the reference to this paper of Prof. Maxwell’s, given by Mr. Tolver Preston, and therefore can speak of it only from his description.

phenomena of solid bodies, but only in one of the three modes of direct impact enumerated above.

(3) Another difficulty arises from the fact that the heavenly bodies are not found to experience any perceptible resistance whatever in passing through this gravity-gas. It is clear that if a body be in motion in the midst of a shower of such particles coming equally from all directions, it will receive a greater number of blows on its front surface, and a less number on its rear surface, than if it were at rest; and consequently its motion will be retarded. The only way of surmounting this difficulty is to suppose that the heavenly bodies, in relation to the gravity-gas, are practically at rest; in other words, that the velocity of the gravity-particles is practically indefinite compared with that of the heavenly bodies. Since in the case of Mercury, for instance, this latter velocity is about thirty miles per second, it is clear that the velocity of the gravity-particles must be something altogether beyond calculation; and then, since the effect of the collisions is, after all, very limited, the mass of the particles must be assumed correspondingly small. Hence our conception of the gravity-gas must practically be that of an indefinite number of indefinitely small particles moving in all directions with indefinitely high velocities—a conception from which it hardly seems safe to draw any definite conclusion whatever.

(4) The last-mentioned difficulty leads to another, viz. to fix the relations between the gravity-gas and the luminiferous æther. They cannot be the same; for Mr. Tolver Preston and Prof. Maxwell have shown * that the velocity of propagation of a wave in such a gas = $\frac{\sqrt{5}}{3}$ × the velocity of the gas-particles. Since the velocity of waves in the æther is about 180,000 miles per second, this would give the velocity of the particles themselves = about 130,000 miles per second—a velocity immensely below what is required to account for the fact of non-resistance. But if the æther and the gravity-gas be different bodies, the particles of the latter must be colliding continually with those of the former, as they collide with the molecules of ordinary matter. How is it that no effects due

* S. Tolver Preston, Phil. Mag. June 1877.

to such collisions are observed? It would seem likely that they would assume the shape of a diffused glow of light and heat, growing more and more intense as the translatory motion of the gravity-particles was turned into vibratory motion of the æther-particles. It is needless to say that nothing in the least resembling this takes place.

We will here leave the discussion of Le Sage's impact theory, as explaining the particular case of gravitation, and go on to inquire how the same, or any other impact theory, can explain some other phenomena of the universe. We will first take those of cohesion.

Cohesion.—To fix our ideas, let us take the case of a square bar of good wrought iron or mild steel, 1 foot long and 1 square inch in area. Then the following two facts, amongst others, have to be accounted for:—

(a) The extension of the bar as a whole (and therefore the extension of the mean distance between the successive layers of its molecules) by $\frac{1}{1000}$ of its length is sufficient to produce between the successive sections of the bar a stress of tension (taking the form of an attraction between the sections) of about 15 tons, say 8000 times the attraction exercised by the earth upon the whole bar when placed in contact with it.

(b) The contraction of the bar through the same relative distance is sufficient to produce between the sections a stress of compression (taking the form of a repulsion between the sections) also of 15 tons or thereabouts.

Can these two facts be explained on any of the three impact theories, which we have shown to be the only possible ones? It seems almost sufficient to ask the question; but it may be well to take them in order.

(1) Can the facts be explained on the hypothesis of direct contact between the molecules? Were this true, it would be impossible to produce any contraction of the bar without forcing two solid bodies into the same space. It is obvious that it will not do to suggest that the contraction may be in the molecules themselves; for then we have only to transfer the inquiry to the particles composing those molecules. Are these particles themselves in contact or not? If they are not, they cannot keep the bar together; if they are, they cannot be compressed. Again, if the molecules are spherical, or of any

other regular shape whatever, they cannot oppose any resistance to separation, *i. e.* there can be no tensional stress. The only way out of this seems to be to conceive them shaped something like burrs, and holding on to each other by hooks. This is altogether contrary to the vortex-atom and all other known theories of molecules. Moreover such burr-like molecules must hold to each other somewhat loosely; and a certain amount of extension would be necessary (as in the case of a slack chain) before any resistance was experienced. But no such slackness has been observed with the most delicate instruments; and we have seen that an extension of $\frac{1}{1000}$ is sufficient to produce an enormous resistance. For these and the like reasons the hypothesis of direct contact is inadmissible.

(2) Can the facts be explained on the hypothesis of particles projected from the molecules of one section against those of the next? Now it is clear that any effect due to this cause will be merely an effect of repulsion. Consequently the end section of the bar will be repelled from that next to it, and will fly off; another body brought into contact with the bar will be repelled by it, &c. For these and the like reasons this hypothesis is inadmissible.

(3) Can the facts be explained on the same hypothesis as that of Le Sage, viz. of independent particles flying through space and intercepted by the molecules of the bar? In the first place, it is clear that these cannot be the particles of the gravity-gas; for if these pass through the earth without having more than a small proportion stopped, it is clear that the number intercepted by an inch of iron will be infinitesimal. We should have to conceive, therefore, a separate atmosphere for each solid body, and an atmosphere the effects of which are many thousand times as great as that of the gravity-gas. But, further, let us assume this atmosphere, and consider what will happen when the bar is extended. Any one section will be removed to a greater distance from the next, and its sheltering influence will be diminished in the inverse ratio of the squares of the distances. Consequently the effect of extension will be to diminish the attraction between the sections; whereas the actual effect is enormously to increase it. For these and the like reasons this third and last hypothesis is also inadmissible.

The two latter hypotheses, and any combination of them, labour under a further and fatal disadvantage, viz. that the cohesion of the bar would be different in different parts. Thus in whatever way the flying particles are supposed to move, it is evident by symmetry that the central section will be solicited in one direction precisely as much as in another; hence the slightest pull will cause the bar to part in the middle.

The above trains of reasoning are not long, and rest on undoubted facts; and the writer has not been able to discover any flaw in them. But unless some such flaw, and a fatal one, be discovered, it must be held to be demonstrated that the phenomena of cohesion cannot be explained except on the hypothesis of action at a distance.

Magnetism.—Of the many difficult cases presented by the phenomena of electricity, it will be sufficient to cite one of the simplest. When an ordinary iron magnet is brought near a piece of iron, the latter is attracted to it. Now the first impact hypothesis is here inadmissible, because the bodies are not in contact; and the second, because the effect is one of attraction, not of repulsion. Thus the only possible explanation of this fact, apart from action at a distance, is by supposing that the magnet intercepts a proportion of a shower of particles which would otherwise impinge equally in all directions upon the iron. It is of course possible to imagine a “magnetism-gas,” different again from both the “gravity-gas” and the “cohesion-gases,” to which this would apply; but the writer has not been able to imagine any property, consistent with the principle of impact, which could be given to the magnet, such as to make it intercept these particles, when the same magnet, before being magnetized, would be unable to do so—and also such as would make it intercept the particles flying towards a piece of iron, and not to intercept the particles flying towards a similar piece of brass.

Vibrations.—Any thing like the vibration of a molecule about a central position (which is the fundamental idea in explaining Heat, Light, and all undulatory movements) seems to be impossible on this theory. For a molecule, once started, is in the position of a free projectile through space, and will continue to move in a straight line until it accidentally strikes against some other molecule which may be moving in any

other direction. Hence it is obvious that the chance of the molecule ever coming back to its original position is indefinitely small. This applies especially to the case of the æther, the particles of which are comparable to those of the gravity-gas.

The above are a few very simple cases, in which it seems certainly difficult to avoid the conclusion that action at a distance must necessarily exist. And if it exists in these cases, then, as already remarked, it becomes at least probable that it may exist in other cases, such as gravity, where the evidence is not so clear. In conclusion it may be asked, therefore, what real reason is there why this hypothesis of action at a distance should not be admitted. To some minds it seems to present itself in the light of a theory which it is *à priori* difficult, if not impossible, to believe. But Physics has nothing to do with mental impressions; and in the history of the Inductive Sciences there are many well-known instances, where *à priori* notions of this kind have seriously hindered the advance of knowledge. It is evident that the progress of science in any direction must be towards certain universal and final facts, beyond which she cannot go. On the one theory, the ultimate fact in the case of gravity is enunciated in a very simple law of force, connecting together all ponderable bodies. On the other theory, the ultimate facts are apparently enunciated in the laws of impact between elastic bodies (which also involve the conception of force), and in the statement of the fundamental conceptions and results of the Kinetic Theory of Gases, assumed to hold for an exceedingly rare gas pervading all space. The writer submits that, *à priori*, one of these theories is as likely as the other—but that both must be judged by the test of their accordance with known facts, and by that test alone must be accepted or condemned.

On the general comparison of the two views, as to their power of explaining facts, one remark may perhaps be allowed. It will not, probably, be denied that, if we only knew the exact laws of any action whatever between bodies, we could at once explain it on the hypothesis that these bodies are made up of centres of force, each possessing position and inertia, and acting on the other centres according to laws which it would be

easy, or at least possible, to determine. It certainly cannot be said at present that we could equally explain any action by the mere laws of impact, even if we include in them those of elasticity. So long as these two statements hold, it seems more in accordance with the cautious spirit of true science to maintain the old theory, than unreservedly to adopt the new one.

XIV. *Note on Prof. Exner's Papers on Contact Electricity.*

By W. E. AYRTON and JOHN PERRY.*

I. IN the autumn of 1879 Prof. Fleeming Jenkin drew our attention to a paper by Prof. Exner, read before the Vienna Academy of Science, and appearing in the July number of their 'Transactions' for that year. This paper will also be found reprinted in this year's April number of Wiedemann's *Annalen der Physik und Chemie*; and quite recently an English translation, prepared by Mr. Brown, has appeared, in the October number of the Philosophical Magazine.

As then, this paper has been deemed of sufficient importance to be printed at least three times; and as the reasoning employed in it is of so plausible a nature as to mislead a casual reader, and to give him erroneous notions on the subject of contact electricity, we have thought it worth while to draw attention to the inaccuracies it contains.

The calculation given in the Phil. Mag. for 1851 by Sir Wm. Thomson of the electromotive force of a Daniell's cell, based on the principle of the conservation of energy, is of course well known. The method employed, which was due to Dr. Joule, is as follows:—The work done by a quantity of electricity Q passing between two points at a difference of potential E is EQ . Now if this electromotive force is produced by a Daniell's cell, the preceding quantity of work must be equal to the energy-equivalent of the chemical changes that take place in this cell when a quantity of electricity Q passes through it. And since this latter can be determined from the heats of combustion of the products decomposed and formed, and from a knowledge of Joule's mechanical equivalent of heat, Sir Wm. Thomson was enabled to

* Read November 13, 1880.

calculate the electromotive force of the Daniell's cell from the supposed known chemical reactions taking place in it. It has been pointed out by Dr. Wright*, and by others, that the great coincidence between the electromotive force of the Daniell's cell, thus calculated, and the value obtained by a direct measurement with an absolute electrometer would not have been arrived at by Sir William had he had at his disposal the more accurate determinations that have since been made of the heats of combustion. This, however, as we think may be gathered from Dr. Wright's paper, does not in the least disprove the accuracy or detract from the utility of Sir Wm. Thomson's, or rather Joule's, theory, but merely shows that the products of combustion in the Daniell's cell are not exactly what have usually been supposed; for it has to be remembered that if energy is developed or absorbed by occlusion of gases, or by any other physical action that has not hitherto been included in chemical actions, this must all be taken into account in the calculation of electromotive force.

II. Now Prof. Exner expresses the opinion that the so-called contact electricity is produced by the oxidation of the metals in contact with the oxygen of the air, in the same way as electricity is evolved by the oxidation of the zinc in galvanic cells. He says he has proved that this is true, and states, in consequence, that the electromotive force between two metals in contact with the air must be measured and expressed by the heats of combustion. The exact relationship which, in his opinion, ought to exist between the contact electromotive force of, say, zinc and copper and the difference of the heats of combustion of equivalent quantities of these metals is the fundamental part of his paper.

He says, at the bottom of page 598, Heft 4, Band ix. Wiedemann's *Annalen*, 1880, as we have translated it:—"We know that in cells each chemical process produces a potential-difference which is proportional to its heat-value; and in the case of the oxidation of a metal in air, we should expect that the potential-difference between a metal and the oxide produced would be proportional to the heat of combustion. Therefore any metal which, when insulated in the air, oxidizes,

* "On the Determination of Chemical Affinity in Terms of Electromotive Force," by C. R. Alder Wright, D.Sc., *Phil. Mag.* April 1880, p. 247.

must contain a certain quantity of separated positive and negative electricity; and it is obvious that these charges are inactive towards outside bodies. These separated electricities cannot surpass a certain tension-difference; for the observed tension is always a constant, no matter if the oxidation continues or not. From this it would appear that the quantities of electricity produced in excess through continual oxidation are neutralized again with the production of the corresponding quantity of heat.

"If now, for example, a piece of zinc through oxidizing in the air has a potential $+E$, the oxidized layer, or rather the layer of air which is in contact with it, has, on the contrary, the potential $-E$; so that the potential-difference is equal to $2E$, which must be measured by the heat of combustion of the zinc. If we now unite the zinc with any indifferent metal, for example platinum, then a part of the electricity will flow over to the platinum until both the metals have a common potential $+P$. The free tension on the zinc becomes now $-E + P$, that of the platinum $+P$; therefore the potential-difference between zinc and platinum is now $-E$, which is measured by half the heat of combustion of the zinc. If, therefore, the heat-value of the Daniell's cell be A (the heat-values, as is well known, must have reference to the chemical equivalents of the substances), and the heat of combustion of the zinc be B , then the potential-difference between zinc and platinum would be equal to $\frac{B}{2A}$. If the metal connected with the zinc is oxidized in the air, the manner of considering the subject still remains the same, or the potential-difference between the metals is measured by half the difference of the heats of combustion."

It will be observed that Prof. Exner speaks of the difference of potentials between a metal and its oxide as determinable from the heat of combustion; we presume, then, this difference must be a constant, what in fact he calls $2E$. Now let us consider the second part of his statement given above; and we find that by joining platinum metalically to zinc the platinum and zinc have a common potential which he calls $+P$; yet the difference of potential between the platinum and the oxide of zinc is now only $+E$, or half the previous

difference between zinc and its oxide. Although, then, he commences by saying that the difference of potential between zinc and its oxide is measured by the heat of combustion, which we know, per chemical equivalent, is a constant, he ends by concluding that the difference of potential is *not* a constant.

But it may be suggested that as his language is a little vague, and not in accordance with that employed in the modern mathematical theory of electricity, perhaps he means that there is a certain charge of electricity in the oxide which is a constant. This, however, does not appear to be his meaning, since a very simple consideration will show that if the charge of electricity in the oxide were a constant, the difference of potentials between zinc and platinum in metallic contact, as measured by the Volta experiments, would not be, as experiment shows, fairly constant for clean dry zinc and platinum (*viz.* 0.981 volt), but would be a variable depending on the condensing-arrangement employed.

[*Addition*, Dec. 21st.—This latter argument, Mr. Brown says, in the 'Electrician' for Dec. 4th, he does not follow. If, however, he will refer to Prof. Exner's own description of the measuring-apparatus employed, he will, by applying the ordinary mathematical laws, see that the method of attaching a Daniell's cell to the zinc and platinum plates in Volta's condenser, first with its poles one way and then reversed, measures, in terms of the Daniell's cell, the difference of potential between a point in the air close to the zinc plate and a point close to the platinum; but cannot possibly give any measurement of the actual electric charge in the zinc oxide or in Mr. Brown's "condensed compound gas-film," or in the platinum plate itself, unless we know the actual distance between the plates forming the condenser.]

III. We are justified, then, in concluding that he means that there is neither a constant difference of potentials between zinc and its oxide, nor a constant quantity of separated electricity. What, then, is his assumption? As far as an attentive study of his paper on our part can lead us, it is simply this:—The potential-difference between two metals in contact in air is measured by *half* the difference of the heats of combustion—an assumption which, in spite of the semblance of reasoning employed in the previous sentences, our

knowledge of electricity gives us no basis for making. But Prof. Exner's sets of experiments I., II., III., consisting of direct measurements with Kohlrausch's apparatus of the electromotive forces of contact of zinc and platinum, copper and platinum, and iron and platinum, combined with J. Thomsen's determinations of the heats of combustion, appear to lend a most powerful support to Prof. Exner's assumption. Are we not justified, then, in accepting it as a conclusion proved by experiment, although it could not have been previously arrived at from our existing knowledge of electricity? Now it is unfortunate for this conclusion that Prof. Hoorweg, in the *Annalen der Physik und Chemie*, No. 9, Band xi. Heft I. pp. 133-155, 1880, has taken exception to Prof. Exner's experiments themselves; and, to make this plain, he gives the following table:—

		Ayrton and Perry			
		Kohlrausch*.	Hankel.	Exner.	(1880).
Zn	Pt . .	0·984	0·984	0·881	0·981
Cu	Pt . .	0·184	0·184	0·367	0·238
Fe	Pt . .	0·384	0·312	0·704	0·369

Our results as given above by Prof. Hoorweg are in terms of a volt, and not in terms of the electromotive force of a Daniell's cell, which is the standard employed by the previous observers. To reduce our numbers to the same standard, they must be diminished by about 10 per cent. They become then:—

		Ayrton and Perry.	
Zn	Pt . .	0·883	} of a Daniell's cell.
Cu	Pt . .	0·214	
Fe	Pt . .	0·332	

From these numbers it will be seen that while Kohlrausch, Hankel, and ourselves, although making the experiments in quite different ways, and with necessarily different specimens of the metals, have obtained fairly consistent results, those of Prof. Exner, with the exception of the

* Prof. Exner says that since the time of Kohlrausch "only isolated and untrustworthy contact experiments have been made." As, however, those even carried out by Kohlrausch himself with metals appear to disagree with those of Prof. Exner, while they agree with the results obtained by other experimenters, Prof. Exner might consistently have included Kohlrausch's name in his sweeping condemnation.

first, stand by themselves. Nevertheless all his results agree with surprising accuracy with the numbers required by his theory.

IV. On page 597 of his paper, Prof. Exner refers to the early experiments of Pfaff, which proved that the measured electromotive force of contact of two metals was independent of the gaseous medium surrounding them, provided, of course, visible chemical action did not take place; and Prof. Exner states that the subsequent experiments of De la Rive, which he thinks proved that chemical action was necessary, negatived those of Pfaff. We have not been able to find any thing about Pfaff in the reference given by Prof. Exner, which is perhaps due to a misprint in the *Annalen*; but Pfaff's letter to Gay-Lussac, which we have come across in the *Annales de Chimie et de Physique*, vol. xli. pp. 236-247, 1829, gives an account of experiments made with as great accuracy as was possible with the instruments in use at the time, and which led to the result that the difference of potential, measured in Volta's way, between zinc and copper metallically connected was not influenced by atmospheres of dry or damp air, oxygen, nitrogen, carbonic-acid gas, hydrogen, and olefiant gas. This is still one of the most valuable papers in the history of contact electricity; and, with all due respect for Prof. Exner's opinion, we are compelled to attach much more faith to the careful work of Pfaff than to experiments of De la Rive, who, we find, actually coated his plates thickly with varnish to prevent oxidation, and, because with such plates he obtained but little difference of potentials, concluded that the well-known Volta effect was produced by oxidation. This experiment, indeed, is only equalled in vagueness by the one described by Prof. Exner at the end of his paper, made with silver in chlorine and silver in air, and which, as has been recently pointed out by Prof. Hoorweg, proved nothing but the well-known fact that silver chloride is an electrolyte. For Prof. Exner's arrangement was this:—"A short glass cylinder was closed air-tight at its upper end with a plate of silver, which did not, however, touch the glass, as there was a collar of paraffin-wax. The bottom of the vertical glass tube was closed air-tight with a cork, through which passed two small glass tubes to admit the gas and allow it to escape, and also a platinum wire

well insulated by paraffin-wax, and the inner end of which touched the silver plate. This latter was only for making metallic connexion with the condenser.

"A second silver plate, of the same dimensions as the first, could be placed on this condenser in the same way as in the earlier experiments.

"Now, if the condenser-plates were connected, there was naturally not the least charge. But as soon as the interior of the glass tube was filled with dry chlorine, the condenser showed at once a considerable and quite constant electromotive force."

Of course it did, we should reply, seeing that a galvanic cell had been formed of platinum, chloride of silver, and silver. If, however, the platinum wire had been soldered to the silver plate, instead of merely loosely touching it, no such effect would have been observed.

Prof. Exner refers to Mr. Brown's most interesting series of experiments*; but we feel that, although carefully made and faithfully described, they cannot throw much light on the relative values of the so-called contact and chemical theories. For Mr. Brown's zinc and copper plates were coated with zinc sulphide, copper sulphide, or zinc chloride and copper chloride; and every supporter of the contact theory is prepared to admit that there is a difference of potential between a metal and its oxide, chloride, or sulphide, or any other of its salts in a dry or wet state. In fact, in Sir Wm. Thomson's earliest experiments on contact, he refers to the great change produced in the measured difference of potentials of a point in the air close to the zinc, and of a point close to the copper, if the copper be allowed to oxidize†. Had Mr. Brown's apparatus enabled him to make quantitative experiments instead of only qualitative ones, his results would have been of great value in connexion with the electromotive forces of galvanic cells such as we have used, in which the ordinary water between the zinc and copper plates is replaced by glass, paraffin-wax, mica, shell-lac, &c.‡,

* "Theory of Voltaic Action," by J. Brown, *Phil. Mag.* Aug. 1878, pp. 142-145, and Feb. 1879, pp. 109-111.

† "New Proof of Contact Electricity," by Sir Wm. Thomson, *Proc. Lit. and Phil. Soc. of Manchester*, Jan. 21, 1862.

‡ "Contact Theory of Voltaic Action," Part II., by W. E. Ayrton and John Perry, *Proc. Roy. Soc.* No. 106, pp. 26-34, 1878.

or by dry metallic salts, such as have recently been employed by Prof. Hoorweg. Mr. Brown's experiments, however, must not be regarded as confuting Pfaff's work of 1829.

V. We are therefore reluctantly compelled to conclude that Prof. Exner's experiments described in his first paper are inaccurate, and that their striking agreement with his assumption is due to a fortuitous combination of errors. And it may be observed in passing, that the same kind of conclusion has been arrived at by Prof. Young, of Princeton, regarding the result communicated to the Vienna Academy of Sciences, that thermoelectricity is also due to oxidation, since he has recently shown* experimentally that the thermoelectric power of metals is the same in air at a millionth of an atmosphere as at ordinary pressures.

We may mention that, for the purpose of testing whether a gas has any important effect at all in contact action, we have for some time been arranging apparatus to try Volta's original experiments in a Crookes's vacuum.

VI. The succeeding paper of Prof. Exner's was given in the last December number of the Transactions of the Vienna Academy of Sciences, and again in No. 6, B. x. H. 2, pp. 265-284, of Wiedemann's *Annalen*. The ideas contained in it are, we think, based on some misconception of the contact theory of electricity. It has long been known that when the dilute acid of a simple cell is saturated with oxygen there is a primary great electromotive force, which diminishes as the evolved hydrogen begins to collect on the negative plate, not finding any more free oxygen to combine with. It has also been known that, if the metal from either plate is carried over and deposited on the other, the electromotive force of the cell goes down. Prof. Exner, however, sets himself to make careful experiments with a Smee's cell, in which deposition of zinc on the negative plate is rendered impossible by having the plates in separate vessels connected with a glass tube drawn out to a fine point; and he found that the primary electromotive force was 1.15 that of a Daniell's cell, and that it diminished after a current produced by short-circuiting had deposited hydrogen on the platinum plate—also that, whatever was the

* "On the Thermoelectric Power of Iron and Platinum in *vacuo*," by Prof. E. A. Young, *Phil. Mag.* vol. x. p. 450 (December 1880).

negative plate, there was the same working electromotive force. "The preceding results," says Prof. Exner, "connect themselves intimately with the consequences of the chemical theory; they contradict entirely the contact theory." For he reasons:—"The contact theory requires that the electromotive force of a Smee's element should begin with a value 0.73 of that of a Daniell's cell" [this is derived from the heat of combustion of zinc in oxygen, the combination of the oxide with sulphuric acid, minus the energy required for the decomposition of an equivalent quantity of water] "and then sink to a lower value, which depends on the amount of polarization—that is, on the amount of resistance,—and, further, that it depends on the nature of the negative plate. The chemical theory, on the contrary, requires that the Smee's element should first have an electromotive force between 0.732 and 2.15 of that of a Daniell" [2.15 is derived from only considering the heat of combustion of zinc with oxygen and the combination of the oxide with sulphuric acid], "and that this value should fall to 0.732 of a Daniell and then remain perfectly constant, no matter what be the metal forming the negative plate, as long as it does not give rise to chemical changes. Further, the value 0.732 of a Daniell must also depend on the resistance of the element."

Now what is correct in this was all given by Sir Wm. Thomson as far back as 1851; but the greater part is incorrect.

First, it is quite a mistake to say that "the contact theory requires that the electromotive force of a Smee's element should begin with a value 0.73 of that of a Daniell's cell." What the "*summation law*"* of the contact theory says is, that the electromotive force of a complete cell is equal to the algebraical sum of all the differences of potential, each measured separately, at the separate contacts—of metals with any layer of gas on them, gas with liquid, one liquid with another, &c.; and what these latter are in a Smee's water element, for example, can be found from the table at the end of our paper†.

* "Contact Theory of Voltaic Action," Part I., by Professors W. E. Ayrton and John Perry, Proc. Roy. Soc. No. 186, p. 23, 1878.

† "Contact Theory of Voltaic Action," Part III., by Professors W. E. Ayrton and John Perry, Phil. Trans. Roy. Soc. part i. pp. 15-34, 1880.

For, taking water, we have

Pt		H ₂ O	.	.	0.285 to 0.345 volt*,
H ₂ O		Zn	.	.	—0.156 „ 0.105 „
Zn		Pt	.	.	0.981 „ 0.981 „
					1.110 to 1.431 volt,
Mean					1.270 volt,

or about what Exner found it for a dilute sulphuric-acid Smee's cell†.

Secondly, as regards the variations of the electromotive force of a Smee's cell, Sir Wm. Thomson calculated‡ from Dr. Andrews's experiments that, if we consider the oxidation of the zinc and the combination of this oxide with strong sulphuric acid, minus the energy necessary to decompose the equivalent quantity of water, we obtain as the electromotive force of a Smee's cell 2,056,200 British absolute units, which corresponds with 0.82 Daniell [with more modern data Exner gives 0.73], since the electromotive force of a Daniell's cell as determined experimentally by Joule is 2,507,100 British absolute units. Sir William adds:—"It is to be remarked that the external electromotive force determined for a single cell of Smee accord-

* The variations observed in measuring the electromotive force of contact of a metal and a liquid are due to the effect of gas absorbed, and being absorbed, by the liquid &c., and will always be noticed if the measuring-apparatus be only sufficiently delicate. Such differences have nothing in common with the great discrepancies referred to at the commencement of this note, on the results obtained by Prof. Exner and by other experimenters for the electromotive force at the contact of metals, since the latter is fairly constant at a constant temperature, so that any great discrepancies in such measurements can only arise from errors in experimenting.

† We are unable, from our results at present published, to calculate exactly the electromotive force of Smee's dilute-acid cell, since, as regards liquids, it was only with distilled water and with strong acids that the electromotive force of contact of platinum was measured in our experiments. We can, however, from these latter approximate to limiting values of the electromotive force of a Smee's dilute-acid cell; that is, using the values of the contact electromotive forces of platinum with water and with strong sulphuric acid, and assuming that the contact of platinum with dilute sulphuric acid is somewhere between these two, it follows that the electromotive force of a Smee's dilute-acid cell, as determined from the sum of the separate contact differences of potential, must at first be greater than 1.567 volt.

‡ "On the Application of Mechanical Effect to the Measurement of Electromotive Forces," by Prof. Thomson, *Phil. Mag.* Dec. 1851.

ing to the preceding principles, by subtracting the chemical resistance" [this latter being due to the evolution of hydrogen upon the platinized silver] "from the value $J\theta\epsilon$, is the *permanent working* external electromotive force. The electrostatic tension which will determine the initial working external electromotive force depends on the primitive state of the platinized silver plate. It could never be greater than to make the initial working force $J \times 1670 \times \epsilon$, or 5,444,500" [2·17 Daniells according to the above reduction], "corresponding to the combination of zinc with gaseous oxygen, and of the oxide with sulphuric acid. It might possibly reach this limit if the platinized surface had been carefully cleaned and kept in oxygen gas until the moment of immersion, or if it had been used at the positive electrode of an apparatus for decomposing water immediately before being connected with the zinc plate; and then it could only reach it if the whole chemical action were electrically efficient, and if there were no chemical resistance due to the affinity of the platinized surface for oxygen.

"It is also to be remarked, that the permanent working electromotive force of a galvanic element consisting of zinc and a less oxidizable metal immersed in sulphuric acid can never exceed the number 2,056,200, derived from the *full* thermal equivalent for a single cell of Smee's, since the chemical action is identical in all such cases, and the mechanical value of the external effects can never exceed that of the chemical action. In a pair consisting of zinc and tin, the electromotive force has been found by Poggendorff to be only about half that of a pair consisting of zinc and copper, and consequently less than half that of a single cell of Smee's."

The alteration in the electromotive force of galvanic cells produced by gas dissolved in the liquid has been known for a long time, indeed before the experiments of De Fonville, De Lérain, Marié-Davy, referred to by Prof. Exner; and we may draw attention to some experiments of our own, which show that the polarization phenomena in voltmeters are wonderfully influenced by the state of the platinum plates and the liquid as regards absorbed gas*

* "A Preliminary Account of Reduction of Observations on Strained Material," &c., by John Perry and W. E. Ayrton, Proc. Roy. Soc. No. 30, pp. 411-435 (1880).

Thirdly, Prof. Exner states that the contact theory requires that the permanent electromotive force of a Smee's should depend on the nature of the negative plate, while the chemical theory requires that it should be independent of the negative metal; further, that his experiments agree with the latter conclusion and disagree with the former. Now the first part of this statement is wrong; for the contact theory does not require *per se* that the electromotive force should, or should not, depend on the negative metal. What the contact theory tells us is that the electromotive force of the cell will depend on the electromotive force of contact of every pair of dissimilar substances in the circuit, and therefore will depend, among other things, on the contact difference of potentials of the negative metal with possibly a gas, the gas with the liquid, the liquid possibly with another gas, the gas with the positive metal, and the positive metal with the negative. Further, the conclusion itself to which Prof. Exner has arrived, viz. that the working electromotive force of a Smee's cell does not depend on the negative plate, has, like his other conclusions, been disputed. For Beetz* has recently published the results of experiments with simple cells; and his electromotive forces are:—

Zinc and platinum.		Zinc and copper.		Zinc and silver.	
Open.	Closed.	Open.	Closed.	Open.	Closed.
1·52	0·72	0·98	0·46	1·23	0·57

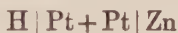
And when he used sodium amalgam the difference of the electromotive forces of the closed cells was equally striking:—

Sodium amalgam and platinum.		Sodium amalgam and silver.		Sodium amalgam and copper.		Sodium amalgam and zinc.	
Open.	Closed.	Open.	Closed.	Open.	Closed.	Open.	Closed.
2·31	1·33	2·05	1·22	1·79	1·14	0·78	0·68

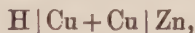
The nature of the negative metal must always have a great effect on the initial electromotive force; we are, however,

* "On the Nature of Galvanic Polarization," by W. Beetz, *Annalen der Physik und Chemie*, B. x. H. 3, pp. 348-371 (1880).

astonished that Prof. Beetz should find such great differences in the columns headed "closed." Our impression has always been that when the negative metal becomes sufficiently coated with hydrogen, the contact between the thin conducting-layer of gas and the metal was almost like that of a pair of metals; and if this is the case, then



is the same as



and almost any negative metal would eventually act like a conducting hydrogen plate.

Prof. Exner's second paper, like his first, we are compelled to regard as wrong theoretically, and describing experiments which do not lead to the conclusions he has deduced from them.

It is not necessary for us to follow Beetz into his disproof of Prof. Exner's statements regarding the use of the word polarization, which is employed in England in the vaguest way to indicate a change of current whether from alteration in the electromotive force or in the resistance, but to which in Germany various philosophers attach distinct meanings. Between the contact theory as properly understood and the chemical theory there is really nothing antagonistic. The "summation law" deduced from various experiments for metals and one liquid, and extended by our own experiments to two or more liquids, tells us that the electromotive force of any arrangement is equal to the algebraical sum of all the separate differences of potential at the various surfaces of contact of dissimilar substances, each difference of potential being measured by an induction method such as we have described and used. The chemical theory tells us that the energy given out in any electric circuit must be equal to the consumption of chemical energy in the circuit. The electromotive force, then, in any circuit can either be calculated on the contact theory, if we know *each of all* the differences of potential at the various surfaces of separation of dissimilar substances (solid, liquid, or gaseous) in the circuit, or it may be calculated on the chemical theory, if we know exactly what are *all* the physical and chemical changes taking place and the heat-equivalent of every one of them. And the amount of the

electromotive force determined in either of these two ways must be identical.

The question of the relative delicacy of the two methods is a totally different question. Any balance accurately made will weigh accurately; but one form of chemical balance is more delicate than another: so, in the same way, there is every reason for believing that an electric test is a far more delicate test of chemical action than the analytical methods employed by the chemist. For example, the action of even small quantities of paraffin-wax on metal, which would quite escape the test of a chemical analysis, we have not only detected, but even measured, with an electrometer*.

XV. *Specific Refraction and Dispersion of Isomeric Bodies.*

By J. H. GLADSTONE, *Ph.D., F.R.S.*†

AMONG the properties of a body which are least liable to change, and which are the most capable of throwing light on its molecular constitution, is its specific refraction. This is the refractive index minus unity divided by the density or $\frac{\mu-1}{d}$.

In early papers on the subject‡, this specific refraction (or "specific refractive energy," as it was then called) was shown to be a constant, unaffected, or nearly so, by change of temperature, by the passage from the liquid to the solid or even gaseous condition, by mixture with other liquids, or by solution, or even (within certain limits) by changes of chemical combination.

In regard to changes of temperature, however, it was observed at the very commencement that there was "some influence, arising wholly or partially from dispersion,"§ which interferes with the exactitude of the law. In order to obviate this, if possible, the calculations were made for the least-refrangible limit of the spectrum, according to the

* "Contact Theory of Voltaic Action," Part II., by Profs. W. E. Ayrton and John Perry, *Proc. Roy. Soc.* No. 186, pp. 26-34, 1878.

† Read on November 27, 1880.

‡ *Phil. Trans.* 1863, p. 323, and 1869, p. 9; *Journ. Chem. Soc.* 1865, p. 108; Landolt, *Pogg. Ann.* cxxii. p. 545; Wüllner, *ibid.* cxxxiii. p. 1.

§ *Phil. Trans.* 1863, p. 323.

formula of Cauchy. But it was found that these gave results little, if at all, more exact than those for the line A of the solar spectrum. In our subsequent work, Mr. Dale and I did not consider it worth while to go through the labour of this calculation; and my observations are always reckoned, if possible, for the line A, whilst Landolt has preferred the α of hydrogen gas, which is identical with the solar line C.

In regard to the passage from one state of aggregation to another, the few cases that have been directly observed are fairly in accordance with the law*.

In the case of mixtures of liquids†, the conclusion that the specific refraction of a mixture of liquids is the mean of the specific refractions of its constituents is a near approximation, if not an absolute truth.

With regard to the influence of solution, some doubt has recently been thrown upon the deductions drawn from dissolved salts or other chemical compounds; but the general, if not absolute, correctness of the method is supported by a very large amount both of direct proof and collateral evidence‡. As an instance of the latter, I may quote the last observations made in my laboratory. The specific refraction of pyrene, $C_{16}H_{10}$, as determined from its solution in benzol, in chloroform, and in carbon disulphide, is respectively

·6235, ·6252, ·6240,

a practical agreement which could scarcely happen if the method were erroneous. Taking the mean of these numbers, and multiplying it by the atomic weight, we obtain, as the refraction-equivalent of pyrene, the very high figure of 126·1.

In regard to chemical combination, it is now well understood that an elementary substance such as carbon will exert the same retarding influence upon the rays of light throughout a very large number of its compounds, whilst in others it may exert a different influence. This has naturally attracted the attention of organic chemists to the subject, and promises to be a very fruitful field of investigation.

In the present communication I intend to confine my remarks to those groups of bodies which exhibit isomerism. It is well

* Phil. Trans. 1869, pp. 10, 11.

† Phil. Trans. 1863, p. 332; Landolt, *Ann. Chem. Pharm.* iv. (Sup. Bd.) 1865, p. 1.

‡ Phil. Trans. 1869, pp. 14, 15.

known that two or more compound bodies, differing from one another in physical or chemical properties, may be composed of the same elements in precisely the same proportions. In such a case the specific refraction may be the same, or it may be different.

It is found to be the same notwithstanding differences of other optical properties, differences of molecular weight, and differences of chemical properties.

1st. *Differences of other optical properties.*—It so happens that among the bodies which display the phenomena of circular polarization, there are several isomeric groups, and that different members of these groups differ from one another in their effect on the polarized ray. Thus with respect to the different terpenes, $C_{10}H_{16}$, some of them rotate the plane of polarization to the right and others to the left, and that to different degrees; yet they have all practically the same specific refraction, 0.537*.

It was also an early observation that solutions of cane-, grape-, and honey-sugar, and gum, of the same strength, though they differ largely in their effect on polarized light, give the same, or very nearly the same, refraction and dispersion†.

Again, it is well known that tartaric acid is an optically active substance, and racemic acid optically inactive, while their chemical composition, $C_4H_6O_6$, is identical. The following table gives the specific refraction and dispersion of these two acids in solution as deduced from data previously published‡. The specific dispersion is the difference between the specific refraction for the line A and that for the line H,

or, which is the same thing, $\frac{\mu_H - \mu_A}{d}$.

	Specific refraction.	Specific dispersion.
Tartaric acid.....	·3020	·0131
Racemic acid.....	·3036	·0143

Carvol and menthol, the odorous principles of caraway and mint respectively, are very definite substances, of the compo-

* Chem. Soc. Journ. 1864, p. 18.

† Phil. Trans. 1863, p. 332.

‡ Ibid. 1869, p. 30.

sition $C_{10}H_{14}O$; but the first rotates the plane of polarization very powerfully to the right, and menthol very powerfully to the left; yet they have practically the same specific refraction*.

	Specific gravity.	Specific refraction.	Specific dispersion.
Carvol from caraway	0.9530	.5126	.0362
„ from dill	0.9562	.5115	.0348
Menthol	0.9394	.5100	.0331

2nd. *Differences of molecular weight.*—Interesting cases of this are to be found among the essential oils, as shown in the subjoined table, in which the numbers given for the *terpenes* are the mean of ten different specimens, for the *citrenes* of twelve specimens, and for the *cedrenes* of eight specimens, each group probably consisting of several isomerides†.

	Specific gravity.	Specific refraction.	Specific dispersion.	Refraction-equivalent.
Terpenes, $C_{10}H_{16}$	0.8600	.5370	.0302	73.03
Citrenes, $C_{10}H_{18}$	0.8466	.5475	.0336	74.46
Cedrenes, $C_{15}H_{24}$	0.9166	.5392	.0307	110.00
Colophene, $C_{20}H_{32}$	0.9391	.5413	.0329	147.23

The terpenes and citrenes show a constant though not a large difference in specific refraction; but the polymeric bodies of the same series seem to have so nearly the same specific refraction as the terpenes that the differences may be attributed to impurities or experimental error. The refraction-equivalents of the three groups are of course very nearly in the proportions of 2, 3, and 4.

3rd. *Differences of chemical properties.*—In the cases already mentioned it is possible that the differences of physical properties depend upon some difference in the arrangement of the ultimate atoms; but there are other cases in which this is perfectly well known to be the case. Isomeric bodies of this nature are more strictly termed metameric. Delffs showed, as far back as 1850‡, that such pairs as formic ether and acetate of methyl, both of the ultimate composition $C_3H_6O_2$, had the same refraction; whilst the papers of Landolt, and the more recent ones of Brühl§, abound in instances. Among the

* Chem. Soc. Journ. 1872, p. 9.

† Chem. Soc. Journ. 1864, p. 18.

‡ Pogg. Ann. lxxxi. p. 470.

§ Liebig's Ann. cciii. pp. 1, 255.

observations in my notebook, hitherto unpublished, occur the following :—

		Specific refraction.	Specific dispersion.
Propyl iodide,	C_3H_7I	·2844*	·0216
Isopropyl iodide,	„	·2883*	
Cresol from thymol,	C_7H_8O	·5116	·0454
Metacresol,	„	·5091	·0452
Benzyl alcohol,	„	·5069	·0415
Nitrobenzoic acid (α),	$C_7H_5(NO_2)O_2$	·3994	
„ „ (β),	„	·4004	
Benzyl butyrate,	$C_{11}H_{14}O_2$	·4777	·0332
„ isobutyrate,	„	·4805	·0331
Monochloro-toluol,	C_7H_7Cl	·4807	·0409
Benzyl chloride,	„	·4836	·0409

Though identity of ultimate composition will generally produce identity of specific refraction, there are certain cases in which isomeric (or, rather, metameric) bodies differ widely in their power of retarding the transmitted ray. The earliest of those observed was the case of aniline and picoline, C_6H_7N ; and as Dr. Thorpe has kindly lent me his specimen of picoline, I am able to confirm the previous determinations.

	Specific refraction.	Specific dispersion.
Aniline	·550	·0635
Picoline (<i>C. G. Williams</i>) ...	·513	·0448
„ (<i>Thorpe</i>)	·522	·0431

The difference in this pair was originally attributed to the fact that the two bodies “are constructed very differently;” and in subsequent papers it was pointed out that, when the atoms of carbon were not saturated in the usual way, there is an augmentation in their refractive power, analogous to what happens when an element such as iron changes its valency†. Brühl has expressed this more definitely by putting forward the theory that, whenever two carbon atoms are doubly linked, there is an increase of the refraction-equivalent amounting to

* Brühl gives the values 0·2873 and 0·2907 respectively for the line C.

† Phil. Trans. 1863, p. 333; Chem. Soc. Journ. 1870, p. 150; Proc. Royal Instit. March 1877.

2.0 for the limit of the spectrum, as reckoned by Cauchy's formula, or about 2.2 for the hydrogen-line α , and of course a little less than 2.2 for the line A. I have no doubt that both Brühl himself and other chemists will have much to say in the future as to the extent to which this theory may be in accordance with present views of the constitution of the various organic compounds.

In my notebook I find the following instances of isomeric bodies which differ in specific refraction:—

		Specific refraction.	Specific dispersion.	Refraction- equivalents.
Acetone,	C_3H_6O	·4420	·0207	25·64
Butyric ether,	$C_6H_{12}O_2$	·4402	·0191	51·06
Allyl alcohol,	C_3H_6O	·4734	·0275	27·45
Carvol,	$C_{10}H_{14}O$	·5122	·0355	76·83
Thymol,	".....	·5206	78·09
Nitraniline (α),	$C_6H_5(NO_2)N$	·469	64·72
" (β),	"	·546	75·34
Cresylic acetate,	$C_9H_{10}O_2$	·4677	·0348	70·15
Benzyllic acetate,	".....	·4945	·0394	74·17
Phenyl-ethyl acetate,	$C_{10}H_{12}O_2$	·4776	78·32
Hydrocinnamene acetate,	".....	·5183	·0382	85·00

Acetone and allylic alcohol have been compared already by Brühl, with similar results, and form one of the striking cases on which his theory depends. The refraction-equivalent of thymol being 6·8 above the normal, is confirmatory of the position which is now given to it in the great aromatic group—a position which I was disposed to assign to it ten years ago, on the evidence of its optical properties.

The two nitranilines were lent to me by Dr. Mills. Unfortunately they are very sparingly soluble bodies; and the above figures, though each of them the mean of three observations, are only given as approximately correct. But that they are really different there can be no doubt.

The two pairs of acetates were lent by Dr. Hodgkinson; and the last one is of particular interest, on account of the cinnamene compound having a higher refraction-equivalent than can be accounted for by any existing theory.

Specific Dispersion.

Though there are several sources of error in determining indices of refraction for the line A or for the line H, the actual distance between these two may be measured with great exactness, and the experimental error rarely, I believe, exceeds 0·0002. The possible error in the determination of the density at the same temperature has also to be considered with regard to specific dispersion; but any inaccuracy in the figures above given will certainly be confined to the fourth place of decimals.

Among the conclusions that may be drawn in regard to dispersion are the two following :—

1st. Where the carbon atoms are exerting a more than normal influence on the refraction of the rays of light, there is a great increase of dispersion. It was pointed out some years ago that the aromatic bodies have a great dispersive power*, and that “dispersion, as well as refraction, increases very rapidly with the number of atoms of carbon that are not combined with at least two of hydrogen or their equivalent.”† Evidence of this is to be found both in the older and the more recent researches, whether in this country or on the Continent, and is always accumulating. Confining our attention to the figures given in this paper, it will be observed that in cases where the carbon is normal the specific dispersion is expressed by low figures (the highest of which is, in fact, acetone, ·0207); while in the isomeric allylic alcohol, which has a higher refraction, it rises at once to ·0275. The essential oils and their congeners, and such bodies as cresylic acetate, are above ·0300; while the purely aromatic compounds are all above ·0400.

2nd. Where isomeric bodies have the same or nearly the same specific refraction for the line A, they have the same also for the line H. The apparent deviations from this rule I am disposed to attribute to experimental error, and still more to impurity of substance. It is clear that in many cases of carbon compounds the presence of a differently constituted body would reveal itself by its influence upon dispersion more than upon refraction.

* Journ. Chem. Soc. 1870.

† Proc. Roy. Inst. March 1877

XVI. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part III.* By C. R. ALDER WRIGHT, D.Sc. (Lond.), Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School.

On the Absolute Values of the Ohm and of the Mechanical Equivalent of Heat, and on the Nature of Polarization and Electrolysis, and the amount of work done when the latter occurs.

55. SINCE the publication of Parts I. and II. of these researches, it has been obligingly pointed out by Mr. L. B. Fletcher, of Baltimore (Phil. Mag. [5] x. p. 436), that, by a slip, it is stated in § 35 that the values of the B.A. unit of resistance deducible from the 1867 experiments of Joule and from those detailed in Part II., are from 1·5 to 2·0 per cent. *above* one earth-quadrant per second, instead of that amount *below* this theoretical value, it being assumed that the mean water-friction value of Joule (41·555 megalergs, § 34) is correct; and Mr. Fletcher also states that the first results of an experimental redetermination of the absolute value of the ohm, on which he is now engaged, are similar in character. Besides the valuations of Lorenz and Kohlrausch, briefly referred to in Part I. as illustrations of the want of absolute certainty as to the true value of the B.A. unit, two other sets of observations on this point have been made within the last two or three years—one by Prof. H. A. Rowland (Silliman's Journal [3] xv. pp. 281, 325, and 430, 1878), and the other by H. F. Weber (Phil. Mag. [5] v. pp. 30, 127, and 189, 1878). By making observations of the value of the current induced in one coil by the establishment of a measured current in another one, Rowland obtained values of the resistance of the former such that, by comparison with four copies of the B.A. unit (or a multiple thereof), the following numbers were obtained as the resistance of the latter:—

				Earth-quadrant per second.
Coil No. 1.	B.A. unit, by Elliot	.	.	0·99257
" 2.	10-ohm coil, "	.	.	0·98963
" 3.	10-ohm coil, by Warden, Mur- head, and Clark	.	.	} 0·99129
" 4.	100 " "	.	.	
	Mean	.	.	0·99098
		.	.	0·99112

* For Part I., see vol. iii. p. 213; Part II., vol. iii. p. 246.

Hence, on the whole, Rowland's experiment indicates an error in the B.A. unit of $0\cdot00888=0\cdot888$ per cent. *in deficiency*.

Weber's determinations, on the other hand, indicate that the B.A. unit is nearly correct, the slight error being one of excess, and that the value of J is somewhat above that deduced from Joule's water-friction experiments. Thus he obtained the following values for J in gravitation measure; the annexed values in ergs are calculated on the supposition that at Zurich the value of g is $981\cdot5$.

	Gravitation measure.	Megalergs.
Value derived from calculations based on the different specific heats of a gas, from experimental determinations by Regnault and Röntgen	428·95	42·10
Value derived from experiments by H. F. Weber, on the heat developed by a known current whilst passing through a resistance measured in absolute mea- sure by himself	428·15	42·02

Taking the mean of these values for J ($=428\cdot55$ in gravitation measure), and determining the heat produced by a measured current in a circuit the resistance of which was measured by himself in absolute units, Weber obtained a mean value for the Siemens unit of resistance of $0\cdot9550 \times 10^9$ C.G.S. units, employing a coil (No. 1914) obtained from W. Siemens as standard. By two other different methods (one depending on the determination of the rate of oscillation of a magnetic needle in a coil, the other on the measurement of the current induced in a given coil by opening a known current in an adjacent circuit) the resistance of this same standard coil was found to be respectively $0\cdot9545 \times 10^9$ and $0\cdot9554 \times 10^9$, giving as final average of the three series of observations, $0\cdot9550 \times 10^9$ C.G.S. units. Unfortunately Weber did not compare his standard Siemens unit with any copy of the B.A. unit: assuming, however, that the Siemens unit used by him bore to the B.A. unit the same ratio as that found by Kohlrausch (§ 36), viz. 1 to $1\cdot0493$, the value of the B.A. unit becomes

finally

$$0.9550 \times 1.0493 = 1.0021 \text{ earth-quadrant per second,}$$

exhibiting an error in excess of $0.0021 = 0.21$ per cent.

Taking these results into consideration along with those of Kohlrausch and Lorenz, discussed in Part II., the following values are finally deducible for the Siemens and B.A. resistance units respectively in earth-quadrants per second:—

	Siemens unit.	B.A. unit.
B.A. Committee	0.9530 (a)	1.0000
Kohlrausch	0.9717	1.0196
Lorenz	0.9337	0.9797 (b)
Rowland	0.9446 (a)	0.99112
H. F. Weber, 1st method . .	0.9550	1.0021 (b)
2nd „	0.9545	1.0016 (b)
3rd „	0.9554	1.0025 (b)

the values marked (a) for the Siemens unit being derived from the observed value of the B.A. unit by dividing by 1.0493, the ratio found by Kohlrausch, and those marked (b) for the B.A. unit being obtained by multiplying the observed values of the Siemens unit by 1.0493. Mr. Fletcher's preliminary results as above stated give a value less than 1.0000. Taking all these valuations into consideration, it would seem that, in the existing state of our knowledge, it is just about as probable that the B.A. unit is in error in deficiency as that it is erroneous in excess. Accordingly, in the following experiments it is assumed that the B.A. unit represents exactly one earth-quadrant per second, and in consequence that the E.M.F. of a Clark's cell is exactly, as determined by him, 1.457×10^8 C.G.S. units, or 1.457 theoretical volt.

56. Admitting this to be so, however, it does not seem to be possible that Joule's water-friction values of J are exact (§ 34): not only do the determinations of Hirn and Violle concur in indicating values for J of from nearly 2 to 3 per cent. higher than these water-friction values (§ 37), but, further, four different sets of observations also indicate that if the B.A. resistance-unit be correct (*i. e.* if it = 1 earth-quadrant per second), or if the Siemens unit be 0.9530 earth-

quadrant per second, the value of J must be from 1 to 2 per cent. higher than these values, and, on the whole, upwards of 42 megalergs. These observations are, first, those of von Quintus Icilius (Pogg. *Ann. ci.* p. 65) as corrected by H. F. Weber (*loc. cit. suprâ*), which were based on an erroneous early determination of the absolute value of a Jacobi resistance-unit by W. Weber; after correction they indicate a value for J of 431·6 in gravitation measure, or, assuming $g=981$, of 42·34 megalergs; and, next, those of Joule himself, those of H. F. Weber above quoted, and those of the author and Mr. Rennie (Part II.), which yield the following results:—

		Value of J , the B.A. unit being supposed to be exactly 1 earth-quadrant per second.	
Von Quintus Icilius (corrected by H. F. Weber)	}	about 42·34 megalergs.	
Joule (1867, <i>vide</i> § 33), the results of which investigation have been shown to be too low (§ 54) . .	}	above 42·10	„
H. F. Weber*, $42·02 \times \frac{1·0000}{1·0021}$. .		41·93	„
Alder Wright and Rennie (value slightly too low)	}	above 41·96	„

Moreover, as stated above, H. F. Weber has calculated, from Regnault's and Röntgen's experiments on the specific heats of air &c., that $J=42·10$ megalergs. Hence, finally, taking into account all the above experiments, the most probable value of J lies close to 42 megalergs, being above rather than below that value. Until further authoritative determinations finally settle the question as to the true values of the B.A. unit and of J , the former may, as above stated, be considered to be exactly 1 earth-quadrant per second, and the latter may be safely taken as being 42 megalergs, most probably lying between 41·75 and 42·25 megalergs. In the following parts of this paper, consequently, J is taken $= 42 \times 10^6$ C.G.S. units,

* Weber's result refers to air-thermometer temperatures, those of the other experimenters to temperatures measured by the mercurial thermometer and not reduced to air-thermometer readings.

$\alpha\chi J$, the factor for reducing gramme-degrees to E.M.F. units (volts), is taken as being $= 0.000105 \times 42 \times 10^6 = 4410.0$.

General Conclusions from the results of previous experimenters, and those subsequently detailed: Statement of Theorem relative to Polarization and the Nature of Electrolysis and the Amount of Work done therein.

57. It has been shown in Part I. (§§ 13–17) that the work expended in decomposing an electrolyte into the “nascent” products of electrolysis is not necessarily the same as that performed in breaking it up into the final products of electrolysis, and that by determining (in terms of E.M.F. or otherwise) the two quantities, conclusions may be drawn as to the general nature of the phenomena connected with the “nascent state.” If the difference of potential between the electrodes of an electrolytic cell be E , during the passage of a quantity of electricity Q sufficient to decompose a gramme of electrolyte in a time t (thereby giving rise to a current $C = \frac{Q}{t}$) a total amount of work $EQ = ECt$ is done, of which $C^2Rt = CQR$ represents the work done as heat due to the resistance of the cell R (Joule’s law, Part I. §§ 1 & 2); consequently an amount $EQ - C^2Rt = (E - CR)Q$ of work is done in decomposing the electrolyte into the nascent products of decomposition. The E.M.F. $E - CR$ representing this amount of work is readily measurable by electrical means; for it is the quantity sometimes spoken of as the “counter E.M.F. set up during electrolysis,” being the value of e in Ohm’s theorem

$$C = \frac{\Sigma(E) - e}{\Sigma(R) + R},$$

where $\Sigma(E)$ is the sum of the electromotive forces of the battery, e the counter E.M.F. set up, $\Sigma(R)$ the total resistance in circuit less that of the electrolytic cell, and C the current produced. For if r be the “resistance of a wire obstructing the current equally with the electrolytic cell” (*i. e.* what may be conveniently termed the *apparent* resistance of the voltmeter, equal to that of a wire through which the current C would pass when a difference of potential E subsisted between its ends), we have

$$C = \frac{E}{r} = \frac{\Sigma(E) - e}{\Sigma(R) + R} = \frac{\Sigma(E)}{\Sigma(R) + r};$$

whence*

$$C \text{ also } = \frac{E}{r-R} = \frac{\Sigma(E)-E}{\Sigma(R)} = \frac{E-e}{R},$$

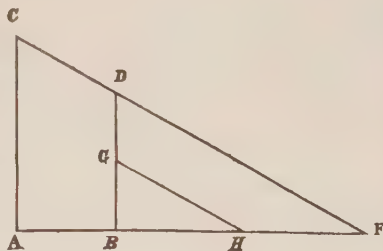
and

$$e = E - CR.$$

58. Very many experiments have been made during the last thirty or forty years on the values of e under varying conditions, on a somewhat closely allied thing, viz. the E.M.F. existent between the electrodes of an electrolytic cell *after rupture of the current*†, and on the E.M.F. of gas-batteries (and especially those with hydrogen and oxygen as gases)‡.

* These relationships may be represented graphically

thus:—On a base-line A B H F let fall perpendiculars A C, B D, representing respectively $\Sigma(E)$ and E , the length A B representing $\Sigma(R)$. Join C D, and produce the line C D till it cuts A B produced in F. Cut off from B D at the end D a length D G representing e ,



and through G draw G H parallel to C D F, cutting A F in H. Then B F represents r , and B H represents R . And by similar triangles,

$$\frac{AC}{AF} = \frac{AC-BD}{AB} = \frac{AC-DG}{AH} = \frac{BD}{BF} = \frac{BG}{BH} = \frac{DG}{HF},$$

or

$$\frac{\Sigma(E)}{\Sigma(R)+r} = \frac{\Sigma(E)-E}{\Sigma(R)} = \frac{\Sigma(E)-e}{\Sigma(R)+R} = \frac{E}{r} = \frac{E-e}{R} = \frac{e}{r-R}.$$

† The term “polarization” is sometimes applied to mean the counter E.M.F. of an electrolytic cell e as above defined, sometimes the E.M.F. set up between the electrodes after the current has ceased to flow (a quantity always less than the value of e existent whilst the current passes), and sometimes (perhaps most frequently of all in a vague undefined sense), to express the fact that something or other takes place tending to diminish the current: thus the silver plate of a Smee’s cell is said to become “polarized.” In the subsequent parts of this paper the terms “counter E.M.F. of an electrolytic cell” and “subsequent polarization” respectively are used to indicate the first two of these meanings.

‡ At the request of the Publication Committee of the Physical Society a discussion of the results obtained by many previous observers bearing in these directions is omitted, together with the numerous references to their

From these researches it results that, other things being equal, the counter E.M.F. set up during electrolysis increases with the current-strength as the size of the electrodes is diminished and as the temperature is lowered, at least within certain limits. The observations made have almost invariably been performed with currents of moderate or considerable magnitude; with such currents in no case has a value for e been obtained less than the E.M.F. corresponding to the decomposition into the final products, whilst with powerful currents much larger values have been obtained: thus with water, all values of e registered lie above 1.50 volt, and sometimes exceed 3 volts (when reduced to that unit). Certain experiments of Andrews (Phil. Mag. [3] x. p. 433), and Buff (*Ann. Chem. Pharm.* xciv. p. 1), made by decomposing water with a feeble battery-power (less than 1.50 volt), appear, however, to show that a less value for e may exist when a very minute current only is employed, in which case simultaneous evolution of hydrogen and oxygen does not take place; if the one or the other be prevented from making its appearance as a free gas by using a large electrode and a minute one (Wollaston's point), a feeble evolution of gas may be noticed (especially at first) from the small electrode, but none from the other. Similarly, the experiments of Helmholtz on what he terms "electrolytic convection" (Phil. Mag. [4] xlvii. p. 152), and analogous observations of others, show that, if the one or the other gas is suppressed by the chemical action of other kinds of gas respectively dissolved in the fluid surrounding the electrode or adherent to the electrode surface, water may be decomposed by an E.M.F. of less than 1.50 volt.

59. As regards "subsequent polarization," or the E.M.F. existent between the electrodes of an electrolytic cell after the original current has been ruptured, even when measured by a quick-working switch or "wippe," it results from the observations at present on record that a more or less perceptibly smaller value is always obtained than corresponds to the counter E.M.F. set up whilst the current was passing.

work. The best *résumé* of this work that the writer is acquainted with is in Wiedemann's *Lehre vom Galvanismus*, which, however, does not include a considerable number of researches published within the last few years.

Under certain circumstances, especially when currents of short duration are employed, the difference becomes very marked; so that on the whole "subsequent polarizations" have been recorded, for acidulated water for instance, of magnitude varying from something upwards of two or even three volts to something less than $\cdot 001$ volt. With currents producing smaller values than $1\cdot 5$ volt (measured immediately after rupture) visible evolution of gas at *both* poles does not seem to have ever been noticed. Recently Exner (Wied. *Annalen*, vi. p. 336, 1870) has shown that to cause visible evolution of gas from boiled-out distilled water, a "subsequent polarization" (measured immediately after rupture by a quadrant electrometer) of from $2\cdot 03$ to $2\cdot 09$ Daniell cells (from $2\cdot 2$ to $2\cdot 3$ volts) must be established; whilst if the water be faintly acidulated, a polarization of about $1\cdot 89$ Daniell = $2\cdot 1$ volts is sufficient. And in the same paper he has also shown that the polarization set up after the current is ruptured differs from the E.M.F. of the battery employed (and *à fortiori* from the counter E.M.F. set up during the passage of the current) only by quantities too small to measure accurately by a quadrant electrometer, when the battery E.M.F. does not exceed from $1\cdot 40$ to $1\cdot 47$ Daniell cell ($1\cdot 54$ to $1\cdot 61$ volt) when larger platinum plates and boiled-out dilute acid are used, and from $1\cdot 94$ to $2\cdot 09$ Daniell cells ($2\cdot 1$ to $2\cdot 3$ volts) with Wollaston's points (platinum wires coated with glass, so as only to expose a minute surface at the ends); whilst with stronger battery electromotive forces than these values the subsequent polarization always falls sensibly short of the battery E.M.F.

60. Various determinations have been made of the E.M.F. which a Grove's gas-battery can generate under various conditions. When the gases are oxygen and hydrogen, it has uniformly been found that the E.M.F. generated is less than $1\cdot 50$ volt, the value representing the work done in the union of ordinary gaseous oxygen and hydrogen to form liquid water, which is the end result of the action taking place in such a cell when it generates a current. Recently Osgood Pierce (Wied. *Annalen*, viii. p. 98, 1879) has found numbers varying from $\cdot 766$ to $\cdot 926$ Daniell cell ($\cdot 84$ to $1\cdot 02$ volt), according to the temperature, the nature of the liquid present, the purity of the oxygen, &c. *Ceteris paribus*, increasing

the temperatures lowers the E.M.F.; Morley has recently shown (Proceedings Physical Society, ii. p. 212, 1878) that when a Grove gas-battery produces a current the E.M.F. is not constant, but is a function of the current produced, being the smaller the greater the current, *i. e.* the less the external resistance, and *vice versa*.

61. A clear coherent explanation of the differences in the numerical values of these quantities obtainable under various conditions, accounting quantitatively for them, and consistent with well-known dynamical principles, does not appear as yet to have been brought prominently forward; the following attempt in that direction is the result of a somewhat prolonged experimental investigation, some of the results of which are detailed subsequently.

Theorem.—Were it possible that the surface-action of the electrodes, the chemical action of substances dissolved in the fluid electrolysed, or of the electrode materials themselves, and other interfering causes (such as the accumulation of fluids of different densities round the electrodes) could be entirely eliminated, *the primary effect of electrolysis would be to break up the electrolyte into "nascent" products, the formation of which would correspond to a definite amount of work, and consequently to a definite E.M.F.*; but the physical attraction exerted by the electrodes upon the nascent products causes a certain proportion of them (variable with circumstances) to be converted *ab initio* into products, the formation of which from the "nascent" products is accompanied by a gain of energy (or evolution of heat). Similarly, under certain conditions the products of electrolysis are chemically acted upon by the electrodes, or by gases occluded upon their surfaces, substances dissolved in the fluid electrolysed, &c.; whilst, as the action proceeds, solutions of different densities accumulate round the electrodes, tending to set up an E.M.F. in virtue of their interdiffusion. All these circumstances modify the amount of work actually performed by the current whilst causing electrolysis, in such a way that *the algebraic sum of the energy gained by these other actions is subtracted from the energy that would otherwise be required to break up the electrolyte into nascent products*.

This theorem may be put in the form of the following

equation.—Suppose that the quantity of total products of electrolysis at the negative electrode be called 1, and out of this amount let $1 - n_1$ parts be evolved “nascent,” whilst n_1 parts are so affected by the condensing or attractive action of the electrode as to be evolved *ab initio* not in the “nascent” condition, but in a more condensed form, viz. in the ordinary physical condition of the substance, if non-gaseous, but, if naturally gaseous, in the form of a more or less condensed form of gaseous matter (occluded gas, quasi-liquefied gas, or gas strongly attracted to the surface of the electrode). Let H_1 be the heat evolved per gramme-equivalent of product in its transformation from the “nascent” to the ordinary free condition, and let h_1 be the heat evolved in further condensing a gramme-equivalent of the substance to the more condensed form in which the fraction n_1 of total product is evolved. Similarly let n_2 , H_2 , and h_2 be the values corresponding respectively to n_1 , H_1 , and h_1 , referring to the products at the + electrode taken as unity. Then the amount of energy to be subtracted from that corresponding to the decomposition into the nascent products due to the attractive action of the electrodes is given in terms of E.M.F. by the expression

$$\{n_1(H_1 + h_1) + n_2(H_2 + h_2)\}\chi J.$$

The energy corresponding to the work done in the decomposition into nascent products being expressed in terms of E.M.F. by E_1 , let $\Sigma(\mathbf{H})$ represent the heat-evolution per gramme-equivalent of substance decomposed, due to the algebraic sum of the chemical actions taking place between the products and the electrodes, &c., and of the diffusive action of the differently constituted liquids surrounding the two electrodes; then the final E.M.F. corresponding to the work done in electrolysis will be

$$e = E_1 - \{n_1(H_1 + h_1) + n_2(H_2 + h_2) + \Sigma(\mathbf{H})\}\chi J.$$

If now E_1 represent the E.M.F. corresponding to the work done in decomposing the electrolyte into the final products, supposing them to escape in the ordinary free condition,

$$E_1 = E_1 - (H_1 + H_2)\chi J;$$

whence

$$e = E_1 + \{(1 - n_1)H_1 - n_1 h_1 + (1 - n_2)H_2 - n_2 h_2 - \Sigma(\mathbf{H})\}\chi J,$$

which may for shortness be written

$$e = E_1 + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J.$$

62. According to the particular values which the several terms in this expression may have, various values for e may be deduced. On examination it is found that all the apparently abnormal variations in the value of the counter E.M.F. set up during electrolysis, of the subsequent polarization, and of the closely allied E.M.F. produced by gas-batteries and analogous combinations may be satisfactorily accounted for by this expression *. Thus, for instance, suppose water to be electrolysed with platinum poles, so that no chemical action takes place between the electrodes and the products, whilst no suppression of hydrogen by the action of dissolved oxygen, or of hydrogen by dissolved oxygen takes place; then $\Sigma(H)=0$. If now the electrode be supposed to be destitute of adherent or occluded gases to commence with, and the current be very minute, the whole of the water decomposed will be transformed into hydrogen and oxygen in a highly condensed form, whence, since $n_1=1$ and $n_2=1$,

$$e = E_1 - (h_1 + h_2)\chi J = E_1 - \Sigma(h)\chi J.$$

Under such conditions therefore *the water will be electrolysed by an E.M.F. less than 1.50 volt* (the value of E_1). Experiment shows in fact that when well-boiled water (either nearly pure or acidulated with sulphuric acid) is decomposed with recently ignited platinum electrodes, an E.M.F. scarcely appreciably greater than 0 will suffice to enable a current to pass, whence $(h_1 + h_2)\chi J$ must, under these conditions, nearly = 1.50 volt,

or $h_1 + h_2$ must nearly = 34,100 gramme-degrees;

that is, *the heats of condensation of oxygen and hydrogen by platinum &c. jointly may amount to almost as large a quantity as that developed by their union to form liquid water.*

That the work done in the condensation of a film of gas by attraction to or occlusion in a solid body is great relatively to the mass of gas condensed is well known. The Author, con-

* At the request of the Publication Committee of the Physical Society, the discussion of several particular cases of this theorem and of their bearing upon and explanation of various phenomena observed by previous experimenters is omitted.

jointly with Prof. W. C. Roberts, has shown (*Chem. Soc. Journal*, 1873, p. 112) that the specific heat of the portion of hydrogen first occluded by palladium is much greater than that of the later portions, the limiting values being near to 9 on the one side and 3·4 on the other—or values respectively representing a condensation to something approaching the liquid state (judged by analogy with liquid bromine, the product of the combining number and specific heat of which is near 9), and a condensation but little exceeding that due to ordinary atmospheric pressure. Presumably when a film of gas is attracted to the surface of a solid, the portions first attracted are very highly condensed, the next ones less so, and so on, a kind of atmosphere or aura surrounding the body being thus produced of density varying from the maximum amount of condensation to the minimum, *i. e.* the pressure of the surrounding atmosphere. The total quantity of gas thus condensed is not inconsiderable: thus an ordinary porcelain or, better still, a platinum crucible, if ignited and cooled in dry air, will weigh less by from one to several milligrammes, according to its size, if weighed immediately it is cold, and before the film or aura of condensed gas expelled by the heat is completely re-formed, than it will weigh if allowed to remain some time in the dry air, and weighed after the aura has been attracted to saturation. The inequality in the deviations from Boyle's law exhibited by gases under high pressures, but when still far removed from their condensing or from their critical points, has been considered by many physicists to be probably largely due to the difference in the attracting or aura-forming capacity exhibited by the tubes and measuring-vessels used, according as the nature of the gas varies. Not only gases, but also liquids, are attracted by solids, forming a layer or aura of highly condensed liquid adherent to the solid: Schliermacher has recently calculated (*Dingler, Pol. Journal*, pp. 224, 471; *Chemical-Society Journal, Abstracts*, 1880, p. 363) that this causes an appreciable error in the determinations of the weight of a unit volume of water hitherto made.

63. When water is electrolysed with non-oxidizable recently ignited electrodes (*e. g.* of platinum), the length of time which must elapse before the electrodes become saturated with gases will depend on circumstances, and amongst others on the fact

that the water will tend to take up oxygen at the + electrode and hydrogen at the - electrode, and the solutions thus produced will diffuse towards the opposite poles, thus tending to set up a double form of "electrolytic convection."

Suppose that a current pass through acidulated water, so that gases are slowly evolved ; if by saturating with oxygen the water surrounding the - electrode the hydrogen is wholly reconverted into water, leaving out of sight the formation of liquids of differing densities round the two electrodes, and supposing that the + electrode and fluid surrounding it are saturated with oxygen, it will result that

$$\Sigma(\mathbf{H}) = \mathbf{E}_1 + \{(1 - n_1)\mathbf{H}_1 - n_1 h_1\} \chi \mathbf{J}$$

(the n_1 , \mathbf{H}_1 , and h_1 , referring to hydrogen), whence

$$e = \{(1 - n_2)\mathbf{H}_2 - n_2 h_2\} \chi \mathbf{J}.$$

Now when $n_2 = 0$ this value is +, being $\mathbf{H}_2 \chi \mathbf{J}$; but if $n_2 = 1$ it would become negative, $= -h_2 \chi \mathbf{J}$: for certain values of n_2 therefore (*i. e.* for certain rates of current-flow, Part IV.), the value of e whilst still + must be less than 1.50 volt ; *i. e.* when "electrolytic convection" takes place, so that the hydrogen evolved by electrolysis is reoxidized as fast as generated, *electrolysis may be produced by means of a less E.M.F. than 1.50 volt.* Obviously the same result follows if the hydrogen be unoxidized, but the oxygen be reconverted into water by dissolved hydrogen ; and the same may ensue if only a part of the hydrogen or oxygen is thus reconverted into water.

64. Again, when $\Sigma(\mathbf{H})$ is negligible compared with the other terms, and n_1 and n_2 are both small, the value of e may be greatly superior to \mathbf{E}_1 ; for when n_1 and n_2 are both = 0 and $\Sigma(\mathbf{H})$ is negligible,

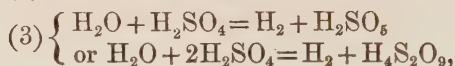
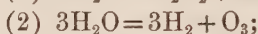
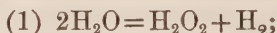
$$e = \mathbf{E}_1 + (\mathbf{H}_1 + \mathbf{H}_2) \chi \mathbf{J} = \mathbf{E}_t.$$

Experiment shows that, *cæteris paribus*, the stronger the current the smaller are the values of n_1 and n_2 ; that is, e continually increases as the current increases, tending towards a limiting value in any given case (Crova, *Ann. Chim. et Phys.* lxxviii. p. 413, 1868). Although at present the data for calculating accurately the limiting values of \mathbf{E}_t for various substances are not extant, yet it is known that in the case of water \mathbf{E}_t must

be upwards of 3 volts; for values of e above 3 volts have been observed: that is, the value of $H_1 + H_2$ is greater than 34,100 gramme-degrees; or *the heat of transformation of the "nascent" products of electrolysis of water into gaseous oxygen and hydrogen jointly exceeds the heat developed by the combination of these gases at ordinary temperature and pressure to form liquid water.*

The theorem therefore accounts for all possible variations in the counter E.M.F. set up during electrolysis, between the minimum values (when the normally gaseous products of electrolysis are evolved not as free gases, but as condensed films of attracted or occluded gas, or when they are chemically acted upon by the electrodes or other substances in contact with them, *e. g.* during the so-called "electrolytic convection" of Hemholtz) and the limiting maximum reached with an indefinitely large current.

65. Before passing from this point it is worth noticing that the circumstance that the limiting value of E_l for water must lie above 3 volts shows that the first action of the current can be neither of the three following changes:—



forming respectively gaseous hydrogen and hydrogen dioxide, gaseous hydrogen and ozone, and gaseous hydrogen and the "persulphuric acid" of Berthelot; for that observer has shown (*Bulletin Soc. Chim. Paris*, 1876, xxvi. p. 56, and 1880, xxxiii. p. 246), that the amounts of heat absorbed by the addition of 8 grammes of oxygen to 9 of water to form hydrogen dioxide, to 16 of oxygen forming ozone, and to sulphuric acid forming persulphuric acid, are respectively 10,800, 14,800, and 13,800 gramme-degrees; so that the transformation of 8 grammes of ordinary oxygen into 8 of ozone would absorb $\frac{14,800}{3} = 4933$ gramme-degrees,

and the above three decompositions would absorb per gramme-equivalent (1 gramme of hydrogen evolved) respectively $34,100 + 10,800 = 44,900$, $34,100 + 4933 = 39,033$, and 34,100

+13,800=47,900 gramme-degrees, corresponding to the setting-up of counter electromotive forces amounting respectively to only 1.98, 1.72, and 2.11 volts, or far below the actual maximum. Even, therefore, if it be admitted that persulphuric acid is the body of which the oxygen that finally escapes is first produced as a constituent, it must be supposed that the hydrogen is evolved as an allotropic modification absorbing heat in its formation from ordinary gaseous hydrogen; whilst if this be admitted for hydrogen, it seems at least probable that the same is true for oxygen, and that the hydrogen dioxide, persulphuric acid, and ozone, found to be formed under certain conditions, are secondary products due to the reaction of the "nascent" oxygen on water or sulphuric acid, or to its "rearrangement" into ozone, just as the oxygen ultimately developed is due to a further rearrangement.

In accordance with the ordinarily received views as to the atomic and molecular constitution of matter, it would seem to result from the fact that the maximum counter E.M.F. set up during electrolysis of water exceeds 3 volts, that the first action of the current is to break up the water (and similarly for other electrolytes) into *free atoms* of the components, which atoms then rearrange themselves into molecules either as a secondary action or under the condensing action of the electrodes, or both; whence it would seem that *the sum of the heat of condensation of hydrogen atoms to molecules together with that of oxygen atoms to molecules exceeds that of the union of the hydrogen and oxygen atoms together to form molecules of liquid water.*

66. The phenomena connected with "subsequent polarization" (§ 58, footnote) are just as readily explained by the theorem as those relating to the counter E.M.F. set up whilst the current is passing. When visible decomposition has taken place for some time, so that the electrodes are surrounded respectively with a saturating aura of hydrogen and of oxygen, varying in density from the highest to the lowest possible value, and when, in addition, there are in the vicinity of the electrodes more or less of the "nascent" products of electrolysis, the counter E.M.F. set up during the passage of the current, and therefore representing the polarization at the

instant of rupture, is (§ 61)

$$e = E_1 + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J.$$

After the lapse of a given interval of time (however small), more or less of the "nascent" products have spontaneously changed into the final products, viz. oxygen and hydrogen, thereby diminishing the value of $\Sigma\{(1-n)H\}$, and consequently lessening the value of e , the "polarization." Even after sufficient time has elapsed for the whole of the "nascent products" to have thus transformed themselves, the diffusion of water containing dissolved oxygen to the hydrogen electrode from the other, and of water containing dissolved hydrogen from the hydrogen electrode to the other, will still cause, by chemical action, a continual removal of portions of the aura of attracted gas round each electrode, thereby causing a continual increase in the mean value of $\Sigma(nh)^*$, and hence a further diminution in the value of e ; finally the polarization must become 0, when

$$\{\Sigma(nh) + \Sigma(H)\}\chi J = E_1 = 1.50 \text{ volt.}$$

Experiments on the rate of diminution of the "subsequent polarization" and the circumstances influencing it are detailed later on (§ 69 *et seqq.*).

67. When an electrolytic cell (*e. g.* a voltameter), the electrodes of which are destitute of attracted films of gas or occluded gases, is connected with an electromotor and a cur-

* Gladstone and Tribe have shown (Chem.-Soc. Journ. Trans. 1878, p. 306) that hydrogen condensed by surface-attraction upon or occluded by certain solids (*e. g.* palladium, platinum, or carbon) exerts a much more energetic reducing action upon various substances than ordinary free hydrogen, the same result for palladium charged with occluded hydrogen (so-called hydrogenium) having been previously observed by Graham (Proc. Roy. Soc. xvii. p. 212, 1869). This result is not due to the condensed hydrogen being capable of evolving more heat by action on the substances in question than would be produced by the same quantity of free gaseous hydrogen, because the reverse is the case, the difference being the heat given out in condensing the hydrogen from the ordinary gaseous condition to the condensed form obtaining in the particular cases in question. The "catalytic" action of spongy platinum exemplified in Dobereiner's lamp, for instance, also illustrates this fact. The effect of the condensation, therefore, is analogous to that of increased temperature, causing chemical actions to take place that would not ensue (at least at any measurable rate) under other conditions, *i. e.* less condensation or lower temperature respectively.

rent of very short duration sent through it, if the amount of decomposition produced be so small that the hydrogen- and oxygen-development equivalent to the quantity of electricity passing are only small fractions respectively of the amount requisite to saturate the electrodes, no visible development of gas will ensue; the polarization at the instant of rupture of current will then be (§ 62)

$$e = E_1 - \Sigma(h)\chi J,$$

the value of h depending on the particular amounts of condensation to which the evolved products are condensed. On passing the current from the same electromotor for the same time again, a slightly less amount of current will flow; for the mean counter E.M.F. set up during this second interval of time will be somewhat greater than that during the first, whilst the total resistance in circuit is the same, whence the current

(which = $\frac{\Sigma(E) - e}{\Sigma(R) + R}$, § 57) must lessen. Similarly, on pass-

ing the current again and again for equal intervals of time, quantities of electricity will pass in each interval, gradually diminishing in amount; whilst the "subsequent polarization" continually increases, the voltameter acting as a condenser, the capacity of which is simply measured by the power of the electrodes to condense upon their surfaces and occlude internally the products of electrolysis. On discharging a charged condenser by causing it to generate a regular succession of currents of equal but very short duration as to time, the quantity of electricity conveyed in each interval must at first be nearly the same, but will gradually diminish. These and various other analogous points in connexion with the behaviour of a voltameter as a condenser have recently been quantitatively studied by Herwig (*Wied. Ann.* ii. p. 601, and vi. p. 305), whose results are perfectly in accordance with the deductions from the general theorem above stated.

68. It is evident that the considerations that apply to the form of voltaic combination produced by the products of decomposition formed by the passage of a current through the decomposing-cell will equally apply if the same products of decomposition are introduced into the cell in other ways; so that if two platinum plates are exposed, the one to water

impregnated with ordinary oxygen gas, the other to water containing dissolved hydrogen, the two waters meeting, the attractive action of the plates will cause a more or less nearly saturated aura to be formed round each plate, and a difference of potential will be set up between the plates representing the work that would be gained by the combination of the condensed oxygen and hydrogen: in fact, the form of Grove's gas-battery thus produced will be identical in all respects with that developed when water is decomposed in a voltameter, except that in the latter case the polarization is more or less enhanced by the presence of the "nascent" products of electrolysis, at least until these have become wholly converted into the ultimate products. Such a gas-battery must therefore develop an E.M.F. expressed by the value of the formula

$$e = E_1 + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J$$

now obtaining; that is, since $n=1$,

$$e = E_1 - \{\Sigma(h) + \Sigma(H)\}\chi J,$$

or, since $\Sigma(H)$ must be extremely small, if not wholly negligible, practically,

$$e = E_1 - \Sigma(h)\chi J.$$

Hence the E.M.F. of a hydrogen and oxygen gas-battery cannot exceed 1.50 volt, which experimentally is found to be the case. Any thing that affects the value of $\Sigma(h)\chi J$ must affect the E.M.F. of a gas-battery; accordingly the E.M.F. is found to vary largely with the temperature, the nature of the plates, the fluid in which the gases are dissolved, the state of concentration of the gas-solutions therein, the presence of other gases, &c.; and in particular it is found to diminish with the strength of the current generated (Morley, *loc. cit. supra*); for the more rapidly the films or auræ of gases attracted and those occluded are used up by chemical action, the less will be the mean densities of the auræ, and hence the greater will be $\Sigma(h)$ and the less the value of e .

Experiments on the Influence of dissolved Gases on the Rate of Fall of the Polarization existent after rupture of the original current (Subsequent Polarization).

69. It results from the general theorem above stated (§ 61), that the rate of fall of the "subsequent polarization" in any

given electrolytic cell (*e. g.* a voltameter) must be more rapid when the circumstances are such as to increase the numerical value of the term $\Sigma(\mathbf{H})$ than when the term is negligible; that is, the rate of fall must be a minimum (under any given conditions) when the fluids surrounding the electrodes (themselves unattacked by the products of electrolysis) have no chemical or physical action on these products, and when the electrodes have attracted and occluded as much of the products as they possibly can, but must be greater when these conditions are not fulfilled; so that in any ordinary voltameter, if the fluid surrounding the — electrode contain dissolved oxygen, the rate of fall must be greater than would be the case if no dissolved oxygen were present to act on the hydrogen aura; whilst, *cæteris paribus*, the larger the electrodes within certain limits, the less will probably be the effect of the oxygen dissolved in a limited amount of surrounding fluid on the hydrogen aura as a whole. Experiments on the rate of fall of “subsequent polarization” have been already made by Ayrton and Perry (*Journ. Tel. Eng.* v. p. 391, 1876), and the results expressed as curves; these observers, however, did not particularly examine the influence of varying amounts of dissolved air &c. on the rate of fall. On the other hand, Helmholtz, Fleming, and others have noticed that when water freed from dissolved air by boiling is electrolysed, the “subsequent polarization” diminishes less rapidly than when water containing dissolved air is employed.

The mode of observation adopted for the purpose of verifying the above deductions from the theorem was much the same as that used by Ayrton and Perry (*loc. cit.*). The electrodes of a given voltameter were connected with an electrometer, a suitable resistance being also in circuit, so that a current of known strength could be passed for any required length of time: to measure the current passing it was found convenient to employ a method based on Ohm’s law, *viz.* reading off the difference of potential set up by the current between the ends of a known resistance by means of a quadrant-electrometer. This method, first, is independent of the errors (due to possible change of zero, horizontal magnetic component, &c.) of ordinary galvanometers, which cannot conveniently be verified without throwing them out of circuit or otherwise varying the

current passing by altering the total resistance in circuit, which is impracticable in experiments in which it is essential that the current should not sensibly vary during long periods of time,—and, secondly, enables the value of an extremely minute current to be determined with as much accuracy as that of a much stronger one, and even with greater accuracy; for whilst the current from a given electrometer is diminished by throwing more and more resistance into circuit, the difference of potential between the ends of the resistance thus thrown into circuit is not only not decreased but is even increased. For if e_1 be the E.M.F. of the electrometer, R_1 the resistance the difference of potential between the ends of which e_2 is measured, and R_2 the resistance of the rest of the circuit, the current passing

$$C = \frac{e_2}{R_1} = \frac{e_1}{R_1 + R_2},$$

whence

$$e_1 - e_2 = CR_2.$$

Hence, as C diminishes e_2 increases, and consequently a larger electrometer-deflection is obtained with a smaller current. Tolerably strong currents develop appreciable amounts of heat in the resistance-wire, thus increasing its resistance and introducing an error in deficiency in the current; so that the method is more particularly applicable for minute currents.

70. The difference of potential set up between the electrodes of a voltameter by the passage of a current C is $E = e + CR$, where e is the counter E.M.F. set up, and R the resistance of the voltameter (§ 57). If R do not exceed 100 ohms (100×10^9 C.G.S. units of resistance), and C do not exceed 0.0001 weber (0.00001 C.G.S. current-unit), the value of CR does not exceed $100 \times 10^9 \times 0.00001 = 0.01 \times 10^8 = 0.01$ volt; whilst, whatever the value of C and R , the E.M.F. equal to the product CR is readily calculable. If now the difference of potential between the electrodes E be read off (in terms of the scale of the quadrant-electrometer) whilst the current is passing, by noticing the deflection of the spot of light from the zero (readings being taken on one side only), and the current be then interrupted, a motion backwards of the spot through a scale-length equivalent to CR will instantly ensue, and subsequently a con-

tinuous motion backwards as the value of e falls; if, however, CR be equivalent to considerably less than half a scale-division of the electrometer, the first sudden motion backwards will be entirely inappreciable. In the following experiments the electrometer was so arranged that 1 scale-division represented about 0.02 volt (readings being taken on one side only of the zero); and consequently as long as CR was less than 0.01 volt (*i. e.* as long as R did not exceed 100 ohms and C 0.0001 weber) the first sudden motion was less than 0.5 scale-division, and was consequently practically inappreciable.

(I.) Surface of each platinum electrode 3.2 square centims. Value of $R=7.6$ ohms; $C=.000005$ to $.0001$ weber; so that CR was quite negligible; value of E at moment of rupture of current = 1.60 volt (average). The following numbers were obtained as the average of a number of concordant observations; the differences between the values obtained on repetition of an experiment were, as might be expected, much greater in the experiments of the A class than in the others.

Fall of E in volts.

Time in seconds since rupture of current.	A. Unboiled acid.	B. Acid well boiled and used as soon as cold.	C. Voltameter charged with acid saturated with hydrogen and oxygen at the two elec- trodes respec- tively.
5	.25	.20	.09
10	.33	.25	.13
15	.39	.32	.15
20	.43	.37	.17
30	.48	.45	.20
60	.59	.58	.26
120	.70	.70	.33
180	.75	.75	.35

(II.) Surface of each electrode 8.0 square centims. Value of $R = 11.2$ ohms, current $.000005$ to $.0001$ weber; so that CR was practically negligible. Average value of E at moment of rupture of current 1.80 volt.

Fall of E in volts.

Time in seconds.	A.	B.	C.
5	·26	·22	·19
10	·33	·27	·23
15	·39	·30	·25
20	·43	·32	·26
30	·48	·36	·28
60	·52	·38	·29
120	·56	·40	·295
180	·58	·41	·30

In precisely the same way analogous numbers were obtained in many other series of experiments, the details of which it is unnecessary to quote. Whether the electrodes were of gold, platinum, or carbon, whatever their size, and whatever the value of E, in all cases the general character of the numbers was the same as in these two examples; i. e. *the rate of fall with acid containing dissolved air was greater than that with acid freed from the greater part of the air dissolved by boiling; whilst this again was greater than that with acid from which the last traces of dissolved air had been removed* (from the fluid surrounding the hydrogen-pole) by the slow evolution of hydrogen therefrom, so as to saturate the fluid with hydrogen and remove the dissolved oxygen by “electrolytic convection.” As the removal of the last traces of oxygen became more and more nearly effected, the rate of fall of polarization (for a given initial value) *gradually approached a minimum value*, beyond which it never sank, this minimum doubtless representing the rate of alteration produced in the auræ by diffusion from one electrode to the other.

71. The following experiments are specimens of a number of other analogous ones, all of which yielded the same general result, viz. that, other things being equal, *the rate of fall of polarization is less the larger the electrode surface*. The volta-meters were precisely like those used in the above experiments, consisting of U-tubes with pieces of platinum-foil bent into cylinders and attached to platinum wires fused into glass tubes which served as mercury-cups—access of external air being prevented by closing each of the two open ends of the U-tubes with a doubly perforated cork (of india rubber, or paraffin),

the mercury-cup tube passing air-tight through one perforation and a delivery-tube (bent over and dipping under mercury or oil) through the other, so that evolved gas could escape without admission of air. The voltmeters, being filled with boiled acid containing about 27 grammes of H_2SO_4 per 100 cubic centims., were then connected with a pair of Minotti cells, a large resistance being in circuit; so that a feeble current passed, evolving one or two cubic centims. of hydrogen per day. After some days (generally a week to a fortnight) the minimum rate of fall of polarization was arrived at; when this was the case, the electrodes were kept for another day at some particular difference of potential, arrived at by suitably altering the current passing and experimented with throughout, and a series of observations made; the electrodes were then again brought to the same difference of potential by passing the current again for some time, and another series of observations made; and so on. Finally, the following values were obtained from several such series of concordant observations, the experiments being alike in every respect save size of electrodes—the strength of the acid and the distance apart of the nearest portions of the electrodes being as nearly as possible the same throughout, and the U-tube being the same; so that diffusion must have gone on at as nearly as possible the same rate throughout. The numbers in the column headed “largest” were obtained with electrodes each exposing 27·5 square centims. surface; those in the columns headed “medium” and “smallest” with electrodes exposing respectively 3·2 and 0·2 square centims. of surface. In every case the value of CR was practically inappreciable.

(I.) Value of E on breaking circuit = 1·60 volt.

Fall of E in volts.

Time, in seconds.	Largest.	Medium.	Smallest.
5	·05	·09	·19
10	·08	·13	·27
20	·10	·17	·37
30	·12	·20	·46
60	·15	·26	·61
120	·19	·33	·75
180	·22	·35	·84

(II.) Value of E on breaking circuit = 1.05 volt.

5	less than	·01	·03	·17
10		·01	·04	·25
20		·02	·05	·31
30		·03	·06	·37
60		·04	·07	·44
120		·06	·09	·49
180		·07	·10	·52

It is evident from these numbers, specimens of many similar experiments, that the predictions from the general theorem mentioned in § 69 are completely verified by experiment. It may be noticed in passing that with the "largest" voltmeter, when the value of E on breaking circuit was below 1 volt, the minimum rate of fall of polarization was so slow that no visible motion of the spot of light occurred even during many seconds, and with still lower values of E even after several minutes.

72. The following experiments are also of interest in connexion with this subject, as indicating how the rate of fall of polarization is affected not only by the removal of the auræ of gas round the electrodes by diffusion from one to the other of fluid containing dissolved gas, but also by the solution of the aura in the fluid itself (if not saturated with the gas constituting the aura), and also by the passage of gas into or out from the interior of the electrode, thus causing a diminution in the aura or *vice versâ*. Platinum- or gold-foil electrodes of various sizes being arranged in U-shaped voltmeters like those just described, a gentle current was passed for some days, so as to saturate as far as possible, not only the liquids surrounding the electrodes with the gases respectively evolved on the electrodes, but also the interior of the foils with occluded gases. The electrodes were then rapidly removed, rinsed with recently boiled just cool acid to remove adherent solution of hydrogen or oxygen, and dipped into a U-tube containing the same recently boiled just cool acid. On connecting the two pieces of foil with a quadrant-electrometer a considerable potential difference was at once indicated. The two pieces of foil were then connected by a shortcircuiting wire for a short time (ten seconds usually); on removal of the wire, the foils being still connected with the electrometer, the spot of light moved regularly for a considerable time, indicating a gradual increase in the E.M.F.

of the voltaic arrangement thus produced, from 0 at the moment of removal of the shortcircuiting wire up to a maximum, which was maintained for some time, after which the E.M.F. gradually fell, precisely as in the experiments just described. It is evident that this development and rise of the E.M.F. set up was due to the formation and increase of an aura of gas round each electrode, the source of which was clearly the gas occluded internally in each respectively, the which gas now passed outwards by a reversal of the process by which it formerly passed inwards. The following three sets of readings (averages of fairly concordant repetitions of each experiment) will serve as specimens of a large number of analogous results; the numbers show the E.M.F. set up after the annexed time had elapsed:—

Voltmeter used	" Largest."	" Largest."	" Medium."
Value of E on breaking circuit in the first instance (had been maintained for several days previously)	1·05 volt.	1·95 volt.	2·20 volts.
Time, after removal of shortcircuiting wire:—	volt.	volt.	volt.
5 seconds.....	·14	·35	·39
10 "	·19	·41	·44
15 "	·21	·43	·47
20 "	·23	·45	·50
30 "	·25	·47	·52
1 minute	·27	·52	·55
2 minutes	·28	·55	·58
3 "	·29	·57	·59
7 "	·29	·59	·60
10 "	·28	·59	·58
15 "	·28	·57	·55
30 "	·27	·53	·50
1 hour	·26	·49	·34
2 hours	·245	·44	·31
3 "	·235	·42	·29
4 "	·23	·40	·28

In these three cases the maximum E.M.F. was attained respectively after about 3-7, 7-10, and 7 minutes. The value of the maximum was much higher in the second case than in the first, indicating a much greater amount of gas occluded, as might be anticipated, since a much more rapid current flowed during the period before the electrodes were disconnected from the battery, the current being near to ·000001 and ·000020 weber during these periods in the first and

second cases respectively. Notwithstanding, however, that a still more rapid current (about $\cdot 000025$) flowed in the third case, the maximum attained was scarcely higher than that in the second, because the smaller surface of the electrode caused the rate of loss of aura by solution in the unsaturated surrounding fluid and diffusion away of the solution thus formed to another part of the U-tube to be relatively larger in this case; consequently the rate of fall after the maximum had been reached was considerably more rapid.

73. A curious effect is sometimes produced by the gradual passage outwards from electrodes of occluded gases and the formation of an aura round each, thus virtually setting up a kind of Grove's gas battery. If the current passing through a voltameter be suddenly largely diminished (but not altogether interrupted) by diminishing the E.M.F. of the battery used, a considerable decrease is brought about in the counter E.M.F. set up in the voltameter; that is, the value of $e = E_1 + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J$ diminishes. The passage outwards of occluded gas from the interior of the electrodes, however, tends to increase the aura round each electrode, and consequently to diminish $\Sigma(nh)$, and hence to increase e ; and the result is that the voltameter behaves for a while like a more powerful opposed battery; so that *the current for a time passes in the opposite direction to that due to the primary electromotor*: of course this effect can only be produced when the E.M.F. of the primary electromotor (after the reduction in its E.M.F.) does not exceed some particular limit. If the experiment be modified by shortcircuiting the electrodes of the voltameter before again coupling them to the battery after reducing its E.M.F., the current will at first pass in the normal direction due to the battery; but as the occluded gases pass outwards from the interior of the electrodes and so form an aura round each, the current passing gradually diminishes in strength until it becomes *nil*, and finally passes in the opposite direction, just as it would have done at first had the voltameter not been shortcircuited. For example, a current of about $\cdot 00005$ weber (capable of evolving about $0\cdot 5$ cubic centim. of hydrogen per day) was passed for several days through a voltameter till the liquids surrounding the electrodes were saturated with oxygen and hydrogen respectively, for which

purpose a battery of two Minotti cells was used. One Minotti cell was then excluded from the circuit, a resistance of 50,000 ohms being included therein (the current being measured by determining the difference of potential set up between the ends of this resistance, as described in § 69), and the voltameter-plates shortcircuited for a few seconds. After removing the shortcircuiting wire, the current passed at a rapidly slackening rate in the direction due to the Minotti cell; but in a very few minutes it ceased to flow altogether, and then began to flow in the opposite direction. The shortcircuiting of the voltameter-plates was then repeated for two minutes, after which the current flowed in the normal direction at a gradually slackening rate: after one hour the current still flowed in the normal direction and had a value of $+0.0000034$ weber; but soon it became reduced to zero again, and then flowed in the reverse direction, having a value of -0.0000017 weber after two hours had elapsed since the second shortcircuiting. After twenty hours more the current was so small that its direction was inappreciable; but on removing the electrodes and igniting them and then replacing them, it flowed continuously in the normal direction. Similar results were obtained in many other analogous experiments.

The gradual setting-up again of an E.M.F. after shortcircuiting the electrodes of a voltameter has been already previously noticed by Ayrton and Perry, and the effect generally compared by them to the residual charge of a Leyden jar; they do not, however, appear to have observed the gradual extinction and reversal of the current just described.

74. It should further result from the general theory of electrolysis above stated, that if the electrodes of a voltameter are shortcircuited whilst still in contact with the fluid saturated with gases surrounding them, on removing the shortcircuiting wire the reproduction of an aura round each electrode will take place much more rapidly than will be the case were the electrodes removed and placed in fresh acid not saturated with gas, as in the experiments described in § 72; for in the former case the loss of aura produced by the passage outwards of occluded gas owing to solution in the liquid will be much smaller than that taking place in the latter case. That this is so the following numbers show, samples of numerous similar

observations made, each series of numbers being the average of several fairly accordant sets of determinations.

(I.) Platinum electrodes, exposing a surface of 27.4 square centims. each, kept at a difference of potential of 1.95 volt in each case for several days before the observations were made, the current passing being near to .00002 weber. Shortcircuited for ten seconds.

Period since cessation of the shortcircuiting.	Electrodes not removed from the acid used whilst the original current passed.	Electrodes removed, rinsed, and placed in fresh acid (recently boiled and just cooled) before shortcircuiting.
During 1st minute .	Steady rise to .86 volt.	Steady rise to .52 volt.
2nd "	Further rise to .95	Further rise to .55
3rd "	" " " 1.03	" " " .56
3rd-5th "	" " " 1.11	" " " .58
5th-10th "	" " " 1.24	Attained maximum .59
10th-20th "	" " " 1.26	Slight fall to .55
20th-30th "	Attained maximum 1.27	Further fall to .53
30th-60th "	Constant at 1.27	" " " .49
60th-120th "	Slight fall to 1.265	" " " .44
120th-180th "	" " " 1.26	" " " .42
180th-240th "	" " " 1.25	" " " .40

(II.) Electrodes exposing a surface of 3.2 square centims. each, kept at potential-difference of 2.20 volts, the current being near .000025 weber. Shortcircuited for ten seconds.

Period since cessation of the shortcircuiting.	Electrodes not removed from the acid used whilst the original current passed.	Electrodes removed, rinsed, and placed in fresh acid (recently boiled and just cooled) before shortcircuiting.
During first 7 minutes .	Steady rise to .60 volt.	Steady rise to .60 volt.
7th-20th minute.	" " " .63	Slight fall to .54
20th-30th "	Constant at .63	Further fall to .50
30th-60th "	Slight fall to .61	" " " .34
60th-120th "	Further fall to .57	" " " .31
120th-180th "	" " .51	" " " .29
180th-240th "	" " .49	" " " .28

75. The absolute mass of gas occluded by even moderately large foil electrodes is but minute ; on Sprengelpumping at a red heat a platinum-foil electrode of about 160 square

centims. total surface (about 16 centims. long, and 5 broad), weighing four grammes, only barely recognizable traces of hydrogen were obtained, even when the electrode had been used for a long time and hydrogen copiously evolved from its surface during electrolysis. The presence of occluded hydrogen, however, can readily be observed by chemical tests, such as the reduction of ferric to ferrous salts, &c. One of the most sensitive was found to be that used by Osann (*Pogg. Ann.* xcv. pp. 311 and 315), viz. washing the electrode (in recently boiled just cool distilled water), and then immersing it in a clear brown-yellow solution of mixed ferric chloride and potassium ferricyanide. In a few minutes, according to the quantity of hydrogen occluded, a distinct blue precipitate forms on the surface of the platinum, due either to the conversion of ferri- into ferrocyanide, or to the reduction of ferric to ferrous chloride, or both together. In this way the presence of hydrogen can be distinguished in a platinum electrode (ignited in oxygen previously to use in the voltameter), even when no visible evolution of hydrogen gas from its surface has occurred, the E.M.F. of the battery used being too small to admit of a steady current passing at a rate more rapid than that representing the rate at which removal of the aura of condensed gas by the effects of diffusion (§ 70) takes place—for instance, when the battery-E.M.F. is not greater than 1.4 to 1.5 volt (Part iv. § 84 *et seq.*). In applying this test, however, too much reliance must not be placed on the formation of a blue precipitate after the lapse of a long time; for organic matters and reducing gases and vapours from the air are apt to be absorbed by the ferric ferrocyanide liquor, causing reduction, especially under the influence of light. Moreover, even platinum recently ignited and cooled in oxygen, when placed in the solution, becomes covered with a thin blue film after a considerable time (some hours or days), suggesting the possible reduction of ferricyanide to ferrocyanide with simultaneous production of platinocyanide. Gold acts in this way much more rapidly than platinum. In applying this test in the above-cited observations, check experiments were always made with a second piece of platinum foil of about the same size recently ignited: the blue deposit on the foil used as electrode was then found

to be notable or considerable when none at all was visible on the check piece.

76. From the general theory of electrolysis and the experiments above described, and the much more numerous analogous observations made but not described in detail for the sake of saving space, it results that the condition of the aura round each electrode of a voltameter that has been used for decomposing water at a given period since rupturing the original current is influenced by many circumstances. The aura round the — electrode, for example, has a particular mean density at the moment of breaking circuit, whilst that round the + electrode has some other mean density, the polarization then existent being governed by the proportions of “nascent” hydrogen and oxygen that were being evolved the instant previously and the mean densities of the auræ, *i. e.* by the values of n_1 and n_2 and h_1 and h_2 in the expression

$$e = E_1 + \{(1 - n_1)H_1 - n_1h_1 + (1 - n_2)H_2 - n_2h_2 - \Sigma(\mathbf{H})\}\chi J$$

(§ 61). After the lapse of a given time, however, more or less of the “nascent” hydrogen and oxygen have rearranged themselves, and more or less of the original aura round each electrode has become reconverted into water by the effects of diffusion (bringing oxygen-containing fluid to the hydrogen-electrode and *vice versâ*) ; so that from these causes n_1 and n_2 have increased, each of these changes diminishing the value of e , the polarization. Simultaneously, however, each aura has been more or less reinforced by the passage outwards of occluded gas from within, each of these changes tending to increase e . Presumably the greater the extent to which the aura was wasted, so to speak, by diffusion, the more rapidly would this outward passage of occluded gases take place ; so that finally the rate of fall of polarization is gradually retarded, first because as the “nascent” hydrogen and oxygen become expended by spontaneous rearrangement this source of fall of polarization regularly diminishes, and secondly because the greater the fall the more energetic is the restoring influence of the outward passage of the occluded gases, at least until the amount occluded becomes materially reduced in quantity. When the amount of fall is such that the rate of outward passage of occluded gases almost balances the rate of wasting of aura through diffusion, the rate of fall of polarization

becomes almost insensible, at any rate for periods of time not too prolonged. This point was reached in many of the experiments, in particular those with the "largest" voltameter and polarizations of values not exceeding a few tenths of a volt (§ 71). Ultimately, however, the occluded gases become exhausted and the auræ diminish to inappreciable quantities, the value of e diminishing to a quantity too small to measure. This result requires an enormous length of time to bring it about by the action of diffusion only; if, however, the voltameter-plates are united by an external connecting-wire, a current flows through that wire, and work is done at the expense of the energy stored up, so to speak, in the auræ and occluded gases of the electrodes. The capacity of the condenser virtually formed by the voltameter-plates simply means the quantity of electricity that can be made to flow in this way, and will approach the more nearly to the quantity of electricity that passed in forming the auræ and charging the electrodes with occluded gases the less has been the waste of auræ by diffusion &c. During the passage of the current, the auræ and the occluded gases are used up by chemical action, just as the zinc is in an ordinary cell; and as their quantity diminishes, the effective E.M.F. of the voltaic couple formed by the plates also diminishes.

If through leakage of the apparatus, or other causes, atmospheric air obtains access to the liquid surrounding the —electrode, the dissolved oxygen thence resulting will of course tend to reduce the aura of hydrogen by a chemical action of a kind akin to the "local action" of an ordinary voltaic element, *i. e.* not contributing to the work done by the current generated. In this case the rate of fall of the "subsequent polarization" (the electrode not being connected by a wire so as to produce a current) will be more or less enhanced above the rate due to diffusion only, as above described (§ 70); whilst if the electrodes are connected and a current is made to pass, the E.M.F. of the voltaic couple thus produced will diminish more rapidly than would be the case were no dissolved oxygen present in the liquid round the hydrogen-plate, just as the zinc of an ordinary cell wastes more rapidly when there is local action than it does when there is not, other things being equal.

PART IV.

[Plate VI.]

On the Validity of Faraday's Law as to the Proportionality between the Mass Electrolysed and the Quantity of Electricity passing; on the Numerical Relationships between the Counter Electromotive Force set up by weak Currents and the Rate of Flow of these Currents; and on the Conditions influencing these Relationships and the consequent Dependence of the E.M.F. of certain forms of Electromotors on the Currents generated by them.

77. The original experiments of Faraday and of many subsequent observers have amply established, for moderately strong currents, the truth of the proposition known as "Faraday's law," or as "Faraday's first law of electrolysis" (Part I. § 7), viz. that when a compound is electrolysed the weight of substance decomposed is sensibly proportionate to the quantity of electricity passing. Still, not only Faraday himself, but also subsequent experimenters have been led to doubt whether this law is rigorously true in all cases, *i. e.* whether it is not possible for very weak currents to pass through certain electrolytes without actually causing electrolysis, or at least without causing an amount of electrolysis precisely proportionate to the quantity of electricity passing. In other words, it has been held that "conduction without electrolysis" may occur in certain cases. On examining the experimental evidence in support of the doubt, however, it does not seem to be at all proved in the cases in which no electrolysis was apparent, even though a weak current passed, that electrolysis did not actually take place, the products being prevented from becoming visible owing either to secondary chemical changes, or other circumstances. More especially in the case of electrolysis of water is this deficiency of proof noticeable; for if the liquid electrolysed were in contact with air before ordinary electrolysis, the hydrogen evolved would necessarily be more or less completely suppressed by the oxidizing action of dissolved oxygen; whilst even in the case of experiments with boiled fluids, or fluids *in vacuo*, the impossibility of getting rid of the last traces of oxygen dissolved in the fluid or occluded in the

electrodes &c. would still affect the quantity of free hydrogen collected, as would also the power of the electrodes to occlude within their material, or to condense upon their surface, the hydrogen that would have appeared in the free state could these actions of the electrodes have been completely eliminated. Moreover it was shown long ago by Buff (*Ann. der Chem. und Pharm.* lxxxv. p. 1, and xciv. p. 15, 1853 and 1855)

that currents in the ratio of $\frac{1}{R}$, $\frac{1}{R+r}$, $\frac{1}{R+2r}$, and $\frac{1}{R+4r}$, when passed through silver solutions deposited quantities of silver sensibly in the same ratio, even when the currents were so minute that the smallest of them only deposited 0.129 gramme of silver in 100 hours, and hence deposited

$\frac{0.129}{100 \times 60 \times 60}$ grammes per second, corresponding to a C.G.S.

current of $\frac{0.129}{360,000 \times 0.01163} = 0.0000308$, or to 0.000308

weber (1 weber = 0.1 C.G.S. current-unit), since 1 C.G.S. current-unit deposits 0.011363 gramme of silver (Part I. § 9). Similarly Buff found that currents capable of depositing from .009 to .113 gramme of silver per 100 hours (.000022 to .00027 weber) evolved quantities of hydrogen usually only differing by less than .05 cubic centim. from the quantities calculated from the current passing when air-free solutions of Glauber's salt, dilute sulphuric acid, or distilled water were electrolysed for from $4\frac{1}{2}$ to 26 hours, so that from 0.11 to 1.09 cubic centim. were collected, the hydrogen pole being a Wollaston point; whilst a just visible evolution of hydrogen was noticeable from a Wollaston point with a yet smaller current, capable of depositing .001 gramme of silver per 100 hours, and hence equal to .0000024 weber. Whilst these experiments indicate that conduction without electrolysis did not take place to any appreciable extent during the electrolysis of the silver salt used, they are yet scarcely precise enough to establish with certainty the same point in the case of water, although they clearly point in that direction. Accordingly the following experiments were made with a view to supplementing Buff's work in this respect.

78. Voltameters were constructed like the one represented in Pl. VI. fig. 1. A U-tube, AB, was drawn out and cut off

in the middle of one of the limbs, and the drawn-out part passed through an indiarubber cork, C, smeared internally with melted rubber to make an air-tight joint. Over this cork (similarly smeared outside) was fixed a calibrated capillary tube widened into a sort of thistle-funnel or bell-mouth D, at the part into which the cork fitted; this tube was bent to a double right angle, so that the part used for measurement, EF, pointed downwards, the lower end passing through an indiarubber cork, H, into a second U-tube, G, the other end of which was closed by another rubber cork through which a stout glass rod, I, passed. The upper U-tube was provided with electrodes, K and L, of platinum-foil of measured size fixed to platinum wires fused through the glass (or sometimes, in the case of the longer limb, supported, as represented in the figure, by a loosely fitting cork in the open mouth of the tube), by means of a platinum wire sealed through a drawn-out glass tube, M, which, being filled with mercury, served as a mercury-cup. In order to fill the instrument, the corks supporting I, and also H, were loosened, and recently boiled, still hot, dilute sulphuric acid poured into the longer limb of the U-tube, AB. This acid rapidly filled this U-tube, and then passed over through the capillary tube, DEF, into the lower U-tube, G, also filling it. A certain amount of acid was allowed to run through the whole instrument, so as to rinse out the first portion poured in, which had probably absorbed air to some extent, after which the cork supporting I was firmly fixed, and then the cork H. If now the two electrodes were connected with a battery, evidently the gases evolved would arise, the one into the bell-mouth of this capillary tube, the other to the surface of the fluid in the longer limb, B, of the upper U-tube. By making K the — electrode, and by working the glass rod I up or down through the cork supporting it, the hydrogen evolved could either be drawn over into the measuring part EF, or forced back again into D; and in this way measurements of the gas contained in D could be readily made. When the quantity of gas collected became too large for measurement, it could be drawn completely over into the lower U-tube, G, so as to empty the bell and capillary tube of gas, by simply drawing out the rod I.

79. In order to saturate the acid in the two limbs A and B with hydrogen and oxygen respectively, as well as to do away with the sources of loss of hydrogen due to traces of residual air and occlusion by the electrode K, a weak current (about $\cdot 0000025$ to $\cdot 000005$ C.G.S. current-unit*, capable of evolving from about 0.2 to 0.5 cubic centim. of hydrogen per day) was passed through the apparatus for several days or even two or three weeks, the evolved hydrogen being from time to time drawn over into the lower U-tube G, and expelled by cautiously loosening the cork H for an instant or two. If during this time measurements were made of the quantity of hydrogen actually collected as compared with that calculated from the current passing (kept as nearly as possible uniform by suitably altering the resistance in circuit, and measured by determining the potential difference set up between the ends of that resistance, as described in Part III. § 69), it was found that a deficiency in the amount collected was always observed, but that that deficiency gradually decreased to a constant minimum. Moreover the period when this constant minimum was first reached was found to be precisely the period at which the rate of loss of polarization observed on breaking circuit reached its constant minimum (Part III. § 70); and it was also precisely the period when the counter E.M.F. set up by a given current with a given apparatus ceased to increase (§ 85). These coincidences, as well as *à priori* reasoning, leave no room for doubt that the cause of the residual constant discrepancy between the observed and calculated amounts of hydrogen is due to that cause of loss of hydrogen which cannot possibly be entirely removed, viz. the diffusion to the hydrogen plate of oxygen-containing liquid, and *vice versa*; whilst the larger deficiencies at first noticed are due to this cause increased by the solution of hydrogen in the fluid, its occlusion by the electrode, and its oxidation by the last traces of unremoved air. That this is the true cause of the residual constant deficiency is moreover further indicated by the fact that the nearer together the electrodes and the wider the

* The currents used in the majority of the experiments described below being only small fractions of a weber, it is more convenient to measure them in millionths of a weber, or *microwebers*. One microweber = $0\cdot 000001$ weber = $\cdot 0000001$ C.G.S. current-unit; so that the above currents are respectively 25 and 50 microwebers.

bore of the U-tube, AB (that is, the more rapid the rate of diffusion), the greater, *cæteris paribus*, is the residual deficiency; whilst fluctuations of temperature, which would necessarily aid the diffusion of the gaseous solutions by setting up convection currents, considerably increase the deficiency. It might be supposed that perceptible errors in measurement of the hydrogen would be occasioned by the adherence to the electrode K of visible minute bubbles of gas; in practice, however, it was always found that gently tapping the U-tube AB caused such bubbles to rise so completely into the bell D, that no visible bubbles still adherent to K could be distinguished.

80. In order to determine quantitatively the amount of loss of hydrogen due to this unavoidable "diffusion discharge" (as for want of a better name it may be termed), a large number of observations were made with the different voltameters employed in the following way. Firstly, a current of 25 to 50 microwebers was passed until the residual deficiency became constant (for a given current); and then the current was gradually diminished at stages of two or three days apart, determinations of the hydrogen actually evolved per day, or per two or three days, being made. By-and-by a particular limiting current-value was arrived at, such that with the particular voltameter used no gas whatever was collected, no matter how long the current was allowed to pass, if the current-strength were below that limiting value; whilst if the current were above that amount, and provided the temperature was as nearly uniform as circumstances permitted, so that this effect of heat-convection currents was reduced to a minimum, a quantity of hydrogen was collected after a given time, the greater the larger the current-value. In this way the following limiting values were obtained with four voltameters, some of the particulars of the construction of which are annexed:—

Voltameter No. 1. Electrodes of platinum-foil bent into cylinders so as to be about concentric with the walls of the U-tube. Total surface of each electrode (reckoning both sides of the cylinder and including that of the piece of platinum wire connected with it to make contact) 27.5 square centims. Average bore of U-tube between the electrodes round the

bend = 1.50 square centim. in section. Distance apart of centres of cylindrical electrodes = 13.0 centims.

Limiting value of current, expressing the rate of diffusion discharge not seriously increased by effects of variation of temperature, = 4.0 microwebers, capable of evolving about 0.04 cubic centim. of hydrogen at 0° and 760 millims. in 24 hours.

Voltameter No. 2. Similar electrodes, each exposing 8.0 square centims. of total surface. Centres of electrodes 8.0 centims apart. Average bore of tube 1.0 square centim. in section.

Limiting value of current 8.0 microwebers.

Voltameter No. 3. Electrodes of foil, each exposing 3.2 square centims. total surface. Centres of electrodes 6 centims. apart. Average bore 1.1 square centim.

Limiting current-value 5.0 microwebers.

Voltameter No. 4. Electrodes of platinum wire, each exposing 0.19 square centim. of total surface. Distance apart 17 centims. Average bore of tube 0.08 square centim.

Limiting current-value 1.5 microweber.

Voltmeters Nos. 1, 3, and 4 contained acid of which 100 cubic centims. contained 27.0 grammes of H_2SO_4 . In the three cases the values of the limiting currents are evidently in the order of the facility with which diffusion would go on—the column of fluid between the electrodes being respectively 13, 6, and 17 centims. long, the first being widest and the last narrowest, whilst the current values are respectively 4.0, 5.0, and 1.5 microweber. The relatively larger value for the limiting current of voltameter No. 2 is explained by the fact that it contained a more dilute and consequently less viscid acid, 100 cubic centims. containing only 1.0 gramme of H_2SO_4 .

The amount of current due to imperfect insulation of the voltameter &c. in these experiments was wholly inappreciable. On connecting the voltameter emptied of acid with a battery of two or three Minotti cells and a resistance of 100,000 ohms, no leakage-current at all could be detected; that is, the difference of potential between the ends of the resistance of 100,000 ohms was less than .005 volt (half a scale-division of the quadrant-electrometer); so that the leakage-current was

less than $\frac{.005 \times 10^8}{100,000 \times 10^9}$, i. e. less than 0.05 microweber, a cur-

rent which would require upwards of five years to evolve 1 cubic centim. of hydrogen from water.

81. The average current passing during any given experiment was determined as follows:—The voltameter having been arranged and the current turned on at a noted time, the difference of potential set up by the current passing between the ends of a known resistance (corrected when necessary for temperature) was determined by means of the quadrant-electrometer; and hence the current passing was known. During the first two or three hours the current usually diminished somewhat, owing to the increasing counter E.M.F. set up in the voltameter; but subsequently it remained sensibly steady, under suitable conditions as to battery-power, temperature, &c. By means of numerous observations the average currents passing in each of various successive periods of time were known; and hence the average current for the whole time was known. Thus, for example, the average currents in one experiment were as follows:—

Period.	Average current during period.
Commencement to 6 hours.	22·4 microwebers.
6 hours to 21 hours	22·1 "
21 " 29 "	21·5 "

Hence the average current for the whole period is

$$\frac{6 \times 22\cdot4 + 15 \times 22\cdot1 + 8 \times 21\cdot5}{29} = 22\cdot03 \text{ microwebers.}$$

In standardizing the quadrant-electrometer, use was made either of a moderately newly constructed Clark's cell, or of one which had "run down" to a known extent as compared with a newly prepared cell*, the E.M.F. of a moderately new

* A large number of experiments made with Clark's cells showed that whilst the E.M.F. of comparatively newly prepared cells (*i. e.* a few days to some three months or so old) is sensibly constant *when suitable precautions are taken in the construction*, yet a gradual decrease in the E.M.F. begins to take place after a longer or shorter time and then goes on continuously. Experiments on the construction and the circumstances influencing the permanence of these cells and others of different kinds, are in progress, which will be described in a future paper; it may be noticed, however, that cells prepared with mercurous-sulphate paste, boiled in a Sprengel vacuum and enclosed in hermetically-sealed glass tubes free from air, appear to be preferable to cells prepared in accordance with Clark's directions with a sealing of melted paraffin-wax (Proc. Roy. Soc. **xx.** p. 444, 1872).

cell being taken from Clark's experiments to be

$$1.457\{1-(t-15) \times 0.0006\} \text{ volt}$$

at t° (*i. e.* the difference of potential set up by the cell between two poles of the same material being expressed by this amount). It hence results that if the value of the B.A. unit of resistance (on which the valuation of the E.M.F. of Clark's cell depends, Part II. § 54) be affected by any error, the values assigned to the current passing in the present experiments are also erroneous in the same ratio. In the majority of the experiments described below the difference in the calculated amount of hydrogen, according as the B.A. unit is assumed correct, or as being ± 0.5 or even ± 1 per cent. in error, is less than the error of measurement of the gas collected, together with the error due to the rate of "diffusion discharge" not being absolutely constantly equal to the values given above, owing to unavoidable fluctuations of temperature.

82. By comparing the quantity of gas collected after the passage of a known average current for a known time with the amount calculated from the current and time by the formula

$$w = (C - C')t\chi$$

(where w is the weight of the hydrogen, C the average current passing, C' the current equivalent to the "diffusion discharge," and t the time in seconds), numbers were obtained according closely together: thus, for example, the observed quantities of hydrogen collected in the experiment cited in § 81 were as follows (voltmeter No. 1 used):—

Period.	Milligramme of hydrogen.
Commencement to 6 hours.	0.004
6 hours to 21 hours.	0.0105
21 " 29 "	0.0055
• Total . .	0.0200

whilst the amount calculated from the formula is

$$(0.000002203 - 0.0000004) \times 29 \times 60 \times 60 \times 0.000105 \\ \text{gramme} = 0.0198 \text{ milligramme};$$

or sensibly the calculated amount was actually obtained, the difference between the two quantities being only 0.0002 milligramme of hydrogen, representing about 0.002 cubic centim.

at 0° and 760 millims., an amount well within the experimental errors.

In precisely the same way the following numbers were obtained in a series of experiments with the same voltameter (No. 1). The currents are given in microwebers (1 microweber $= 0.0000001$, or 1×10^{-7} C.G.S. current-unit) in the first column, and the time in hours in the second; the third column gives the value of $Ct\chi$, and the fourth of $(C-C')t\chi$, the two sets of values being given in order that the amount of suppression of hydrogen due to "diffusion discharge" may be rendered manifest.

Average current, in microwebers.	Time, in hours.	Weight of hydrogen, in milligrammes.		
		Total calculated from quantity of electricity passing.	Previous amount, less that due to "diffusion discharge."	Observed amount.
380	30	·432	·428	·43
285	20	·216	·213	·21
200	23	·174	·170	·17
90	24	·082	·078	·076
80	42	·127	·121	·120
48	17	·030	·028	·027
47	42	·075	·069	·068
24	22	·020	·017	·017
22.0	29	·024	·020	·020
9.7	43	·016	·009	·009
4.7	48	·009	·001	·001
Less than } 4.0	{ Various periods up to 192 hours.	—	nil.	nil.

Similarly, the following numbers were obtained with voltameter No. 2:—

750	1.25	·050	·049	·049
285	6.25	·067	·065	·063
191	5.25	·038	·036	·035
122	4	·018	·017	·016
113	21.25	·090	·084	·081
59	22.5	·050	·043	·041
34	23.5	·029	·022	·022
21.0	23	·018	·010	·010
17.0	55	·036	·018	·019
16.3	46	·030	·016	·016
Less than } 8.0	{ Various periods up to 100 hours.	—	nil.	nil.

With voltameter No. 3 the following numbers were obtained:—

220	16	·133	·130	·130
65	24	·052	·048	·045
50	47	·089	·081	·080
6·3	41	·010	·003	·004
Less than } 5·0	{ Various periods up to 240 hours.	{ —	nil.	nil.

And with voltameter No. 4 the following numbers:—

23·0	21	·018	·017	·017
20·0	24	·018	·017	·017
7·0	46	·012	·009	·009
Less than } 1·5	{ Various periods up to 100 hours.	{ —	nil.	nil.

In nearly every instance the observed quantities of hydrogen and those calculated from the quantity of electricity passing, after subtracting the amounts due to “diffusion discharge,” either coincide or do not differ by more than ·001 milligramme of hydrogen, or about 0·01 cubic centim., an amount of variation not outside the probable errors of measurement. In the few cases where the difference reaches ·002 or ·003 milligramme, the observed amount is always less than the calculated quantity, the cause being that the temperature could not be kept absolutely uniform, and consequently the loss of hydrogen by “diffusion discharge” is a little underestimated, the normal value of the rate of diffusion discharge being a little increased through the effects of heat-convection (§ 79). Some half dozen other experiments were made in which slightly greater differences were observed, always in the same direction, viz. deficiency in the amount of hydrogen collected; in these experiments the temperature fluctuated more than in those above cited, and hence the results are not quoted, being vitiated by the increased effect of heat-convection.

From these numbers the final conclusion may be fairly drawn, that *when water is electrolysed the mass decomposed is always proportionate to the quantity of electricity passing*, no matter how great may be the time it takes to pass, *i. e.* no matter how small is the actual current employed, thus confirming and amplifying the results obtained by Buff

above quoted ; so that the universal validity of Faraday's law may fairly be taken as being established. On the other hand, the recent experiments of Guthrie and Boys (Phil. Mag. [5] x. p. 328, Nov. 1880) show that a glass vessel filled with dilute sulphuric acid or other electrolyte, and suspended by a wire in a rotating magnetic field, is urged to a move by a force producing torsion in the wire varying as the product of the conductivity of the electrolyte into the relative speed of the magnets compared with that of the fluid set rotating whirlpool-fashion inside the glass vessel by induction ; and it is supposed by the authors that, in this case, no electrolysis occurs, although currents circulate in the fluid. The absence of electrolysis, however, in these experiments, is not only unproved but is highly improbable. At any given instant any two opposite points on the inner surface of the glass containing-vessel in contact with the liquid will exhibit a greater or less difference of potential, and a current will flow between them through the liquid, the points on the glass surface acting as electrodes ; after a half revolution the potentials of the two points are reversed, the current flowing in the opposite direction relatively to the points (but in the same direction relatively to the magnets) ; so that so far as these two points are concerned a series of alternating currents (or rather of currents going through a regular cycle increasing from 0 to a + maximum, decreasing to 0 and then to a — maximum, and then increasing again to 0, and so on) are set up, the effect of which is to eliminate the effects of "polarization" as completely as in Kohlrausch's method of determining conductivity by means of alternating currents, the products of electrolysis being reunited, so to speak, by the action of the reverse current before they have time to escape. Since the nett chemical action is nil, the work done by the currents appears solely as heat ; but it does not therefore follow that electricity passes through the liquid without causing electrolysis, any more than in Kohlrausch's experiments.

Relationships between the Counter Electromotive Force set up during Electrolysis and the Rate of Flow of the Current passing.

83. It has often been noticed by previous observers that the so-called "polarization," or, more strictly, counter E.M.F.

(§ 57) set up during electrolysis, especially of acidulated water, by a given current, gradually rises until it becomes approximately constant. The cause of this is doubtless that so long as the fluid surrounding the hydrogen-electrode contains dissolved air, and so long as the electrodes and the fluids surrounding them are capable of further attracting, occluding, or dissolving the gases evolved in their proximity, the aura surrounding each electrode does not possess its normal average density ; that is, the values of $\Sigma(nh)$ and $\Sigma(H)$, in the expression for the counter E.M.F. set up (Part III. § 61),

$$e = E_1 + [\Sigma\{(1-n)H - \Sigma(nh) - \Sigma(H)\}]\chi J,$$

are greater at first than the values to which they finally subside.

For the same reason, if an electromotor of E.M.F. not greater than 1 to 1.5 volt or so be connected with a voltmeter containing diluted sulphuric acid (unboiled, or even if boiled), and provided with electrodes of non-oxidizable material, as is well known, a current flows at first, the strength of which gradually diminishes to a minute amount, whilst the so-called "polarization" of the voltmeter increases until it differs from the E.M.F. of the electromotor by only a very minute quantity. With boiled acid, and especially in voltmeters so constructed that neither the oxygen evolved at the + electrode nor the external air can reach the - electrode (saving by unavoidable diffusion), the rate of the diminution of the current is much greater than is the case when these conditions are not fulfilled. On trying experiments of this class, however, it was found that even with the most carefully constructed voltmeters the current never became too small to measure, even after many weeks ; it gradually subsided to a limiting value, below which it never sank (*i. e.* as long as the E.M.F. of the electromotor and the resistance of the circuit remained the same). No trace of gas, however, was evolved at either electrode ; which was evidently due to the fact that, owing to "diffusion discharge," the hydrogen and oxygen evolved by the current became reconverted into water just as rapidly as they were generated by the current ; so that the particular final steady current attained with any given apparatus measured the rate of diffusion discharge with that apparatus under the particular conditions of the experiment.

84. On comparing such results with different electromotors, it was at once perceived that when the resistance in circuit remained the same, the greater the E.M.F. of the electromotor the greater was the value of the final steady current that passed, although as long as the E.M.F. of the electromotor did not exceed a certain limiting value (different for each form of apparatus) no visible evolution of gas took place in any case; *pari passu* with the increase in the strength of the current, the counter E.M.F. set up was found to increase; that is, the value of $e = E - CR$, where E is the difference of potential between the electrodes, C the current, and R the resistance of the column of fluid between the electrodes (Part III. § 57). Thus the following values were obtained with voltameter No. 1 above described (§ 80), and precisely analogous ones with the others.

Final steady current.	Value of e .
0.1 microweber.	0.140 volt.
0.13 ,,	0.297 ,,
0.24 ,,	0.468 ,,
0.5 ,,	0.615 ,,
0.8 ,,	0.929 ,,
1.2 ,,	1.395 ,,
2.3 microwebers	1.523 ,,
3.1 ,,	1.564 ,,
4.0 ,,	1.663 ,,

With this particular voltameter currents of greater magnitude than four microwebers caused an evolution of hydrogen (§ 80); with currents less than this amount none was obtained. Since the values of the counter electromotive forces set up by these currents were considerable, especially when the current was near the limiting value of four microwebers, it results that the hydrogen which combined with the oxygen diffusing to the $-$ electrode, and the oxygen combining with the hydrogen that diffused to the $+$ electrode, was the gas occluded within or condensed upon each electrode respectively, and not that produced by the electrolysis reoxidized *pari passu* with its formation; for in the latter case the nett work done as electrolysis during the passage of this current would be *nil*, and hence e would $= 0$. The action of the "diffusion

discharge" is therefore precisely like that of dissolved air present in the fluid electrolysed in the first instance (§ 76), comparable with the "local action" of an ordinary cell. In any given experiment the value of e will rise (the current remaining constant) until the rate of diminution of aura at each electrode due to this cause just balances the rate of increase through electrolysis. As this latter rises when the current is increased, so will the mean aura-density rise, and the amount of aura dissolved away from the electrode by the surrounding fluid in a given time, and consequently the rate of diffusion discharge, until the aura is at its maximum mean density, *i. e.* saturated, after which a further increase of the current simply causes free gases to escape. In this case the value of e is still found to increase with the current, obviously indicating that the values of the n 's (*i. e.* of the fractions of hydrogen and oxygen not evolved in the nascent state *ab initio*) decrease as the current increases. Similarly, when the temperature falls the value of e rises (*cæteris paribus*) and *vice versâ*, indicating that a fall in temperature increases, and a rise decreases, the fractions of gases evolved "nascent" in the first instance.

The following experiments were then made with the view of investigating the effects produced in the value of e (that is, in the values of the n 's) by altering certain of the conditions of electrolysis.

Effect of Alteration of the Size of the Electrodes.

85. It would seem *à priori* probable that whilst e increases with the current when the electrodes are the same, and decreases when the size of the electrodes is increased, the current remaining the same, it will remain constant if the current and size of electrode increase in the same ratio, so that the rate of flow of electricity per unit of electrode-surface (sometimes spoken of as the "density of the current") is constant. The following experiments show that this is so.

The voltameters used were mostly those described above (§ 78), or others of similar construction, only differing in that the measuring-tubes were replaced by ordinary fine tubes bent over and dipping under mercury or water, so as to allow of the evolved gas escaping without introduction of

air—a similar arrangement being applied at the limb containing the + electrode (as described in Part III. § 71). They were filled with boiled dilute sulphuric acid of such strength that 100 cubic centims. contained 27.0 grammes of H_2SO_4 (in other experiments different strengths of acid were employed), and then submitted to the action of a current of 25 to 50 micro-webers for several days, or even weeks, until the rate of fall of the polarization noticed after breaking battery-contact became sensibly constant at its minimum value for the particular current passing (§ 70), at which time, as already stated (§ 79), the difference between the hydrogen actually collected and that calculated from the quantity of electricity passing also became reduced to the constant minimum. During the time that elapsed since first starting the experiment, observations of E , the difference of potential between the electrodes, were frequently made: the current C passing being also determined by observing the difference of potential set up between the ends of a known resistance also in circuit (Part III. § 69), and the resistance R of the voltameter being known from the dimensions of the column of liquid between the electrodes and its specific resistance (as determined by Kohlrausch and others), the value of $e = E - CR$, the counter E.M.F. set up, was known. It was invariably found that the value of e continually rose after first starting the experiment until it finally reached a constant maximum, the time when this maximum was reached being precisely coincident with the epoch when the minimum rate of fall of polarization and the minimum deficiency in hydrogen collected were attained.

Thus, for example, the following numbers were obtained with voltameter No. 1, when filled with acid containing 40.0 grammes of H_2SO_4 per 100 cubic centims., the values being calculated by interpolation from experiments in which the current was uniformly near to the value 1000 microwebers = 0.0001 C.G.S. current-unit.

Counter E.M.F. set up for a current of 1000 microwebers.

Freshly boiled acid just cool; values obtained during first few minutes of passage of current.	} Values gradually increasing up to 1.965 volt.
--	---

After passage of a current of about 300 microwebers for two days, so as to evolve some 5 cubic centims. of gaseous hydrogen, and nearly saturate the voltameter-liquid with oxygen and hydrogen in the two limbs respectively.	Values gradually rising from 1·965 to 2·150 volts.
After another week's passage of a current of about 50 microwebers.	Values rising from 2·150 to 2·250 volts.
Constant maximum attained after a fortnight's passage of the current.	2·267 volts.

86. In precisely the same way analogous numbers were obtained with the same voltameter and different currents, or different strengths of acid, and similarly with the other voltameters. It was found that when the sources of loss of hydrogen other than diffusion discharge were wholly eliminated, the value of the counter E.M.F. set up with a given current not only remained constant as long as the current did not vary, but also was the same if the current was varied through a considerable length of time (whilst making other observations), and then brought back to the original amount. With feeble currents of strength not exceeding a small number of microwebers per square centimetre of electrode-surface, however, the value of e was found to be very sensitive to causes which would act on the equilibrium of the auræ surrounding the electrodes, especially to changes of temperature which would increase the normal effect of diffusion discharge by setting up heat-convection currents; so that the constant E.M.F. due to the original current was often not absolutely (but only approximately) arrived at until after the lapse of some hours. For this reason too, the counter E.M.F. observed was often less by 1 or even 2 or more per cent. in such cases when determined in the afternoon (in the warmest part of the day) than when determined the first thing in the morning—partly because the actual rise of temperature diminished its value, but more particularly because of the increased effect of heat-convection in affecting the auræ. In making the following determinations, therefore, the mode of procedure adopted was as follows:—The voltameter having been saturated with hydrogen

and oxygen in the two limbs respectively by a fortnight's passage of a current of some 50 or 100 microwebers, a particular current was adjusted to pass by applying a given battery (of Minotti, De la Rue and Müller, Leclanché, or other cells, as most convenient, but chiefly the three first), and introducing a given resistance into the circuit to measure the current with. The whole was then left to itself till the next day, when a number of careful observations of the current passing and the value of E were made at as early an hour as possible (usually about 9 o'clock), so that the effect of the heat-convection currents due to alteration of laboratory temperature should be a minimum. The particular temperature of the measuring resistance-coil (platinum-silver or German-silver wire) being known, its resistance in ohms R_1 was known; and the potential-difference in volts E' being known by standardizing the scale of the electrometer by a Clark's cell, the current was known in C.G.S. units, being given by the formula

$$C = \frac{E' \times 10^8}{R_1 \times 10^9}.$$

The resistance of the voltameter, R , being known, the value of $e = E - CR$ was thus known (usually the term CR was negligible, or at least small compared with E). The current was then allowed to pass for 24 hours, and the observation repeated as early as possible in the day, and so on. Usually the results of consecutive days' measurements agreed extremely closely. When a sufficient number of daily determinations had been made, the resistance in circuit was altered so that a different current passed, and another series of determinations lasting over some days made, and so on. Sometimes after making various series of determinations of the relative values of C and e in this way, the value of C was brought back to nearly the same value as that possessed in observations of several days or weeks before. In such cases the values deduced in the second set of observations were sensibly the same as those formerly obtained; or at least they uniformly corresponded to points lying sensibly on the same mean curve, obtained by plotting the currents as abscissæ and the values of e as ordinates. Thus, for instance, the average of three closely accordant sets of consecutive morning readings with voltameter no. 1 (containing acid of which 100 cub. centims. contained 40.0 grammes H_2SO_4), made near the beginning of a

long series of determinations lasting over many weeks, and that of three other sets of accordant observations made near the end of the period, gave the following numbers—

Earlier series.		Later series.	
Current in micro-webers.	e in volts.	Current in micro-webers.	e in volts.
23.5	1.906	22.3	1.901
21.0	1.892	20.1	1.895
20.6	1.880	19.8	1.870
Average 21.7	1.893	20.7	1.889

thus giving the final average—Current = 21.2, e = 1.891.

Similarly with voltameter no. 4, containing acid of which 100 cubic centims. contained 27.0 grammes H_2SO_4 , the averages of two similar series of daily observations, near the beginning and end respectively of a lengthened period of time during which the curve-values were being determined, were as follows :—

	Current in microwebers.	e in volts.
General average from early series.....	4.70	2.334
" " " later " 	4.85	2.337
Mean.....	4.77	2.3355

and so on in dozens of other analogous cases.

87. The following tables give the final averages deduced from four lengthened series of daily morning observations made with voltameters nos. 1, 2, 3, and 4 above mentioned (§ 80), containing acid of such strength that 100 cub. centims. contained 27.0 grammes of H_2SO_4 . The average temperature of the different series of experiments was in each case not far from 18° , near to which temperature the specific resistance of dilute sulphuric acid was found to be as follows by Kohlrausch and Nippoldt (*Pogg. Ann.* cxxxviii. p. 379, 1869):—

Sp. gr. of acid.	Percentage of H_2SO_4 .	H_2SO_4 per 100 cubic cen- timetres.	Specific resistance at 22° .	
			Mercury = 1.	Absolute (C.G.S. system).
1.1431	20.2	grammes. 23.1	14990	1.424×10^9
1.2045	28.0	33.7	13133	1.247×10^9

the numbers in the last column being deduced from those in the preceding one by taking the specific resistance of mercury on the C.G.S. system as being 0.000095×10^9 , i. e. 0.000095 ohm per column of 1 square centim. in section and 1 centim. long; whence, by interpolation, the specific resistance of acid containing 27.0 grammes H_2SO_4 per 100 cub. centims. is, at 22° , 1.31×10^9 . The numbers obtained by Kohlrausch (*Pogg. Ann. Ergbd.* viii. p. 1, and clix. p. 233, 1876) yield a slightly different value, about 12 per cent. higher.

Sp. gr. of acid.	Percentage of H_2SO_4 .	H_2SO_4 per 100 cubic centimetres.	Conductivity at 18° . Mercury=1.	Specific resistance at 18° (C.G.S. system).
1.1414	20	grammes.		
1.1807	25	22.8	.00006108	1.556×10^9
		29.5	.00006700	1.417×10^9

whence acid of 27.0 grammes per 100 cub. centims. would have a specific resistance of 1.47×10^9 at 18° .

The value obtained by Paalzow for acid represented by H_2SO_4 , 14 aq. (*Pogg. Ann.* cxxxvi. p. 489, 1869), was 14157 times the resistance of mercury at 19° . This acid contains 28.0 per cent. of H_2SO_4 , representing 33.7 grammes per 100 cub. centims., possessing the specific resistance 1.34×10^9 , or about 8 per cent. higher than that found by Kohlrausch and Nippoldt.

On the whole the specific resistance of acid of the strength used, viz. 27 grammes per 100 cub. centims., may be taken as 1.4 ohm at 18° , whence the values of R for the four voltmeters, calculated from the dimensions of the columns of fluid between the electrodes (§ 80), are:—

$$\begin{aligned}
 \text{Voltmeter No. 1.} & \quad \frac{13 \times 1.4}{1.5} \text{ ohms} = 12.1 \text{ ohms.} \\
 \text{,, No. 2.} & \quad \frac{8 \times 1.4}{1.0} \text{ ,,} = 11.2 \text{ ,,} \\
 \text{,, No. 3.} & \quad \frac{6 \times 1.4}{1.1} \text{ ,,} = 7.6 \text{ ,,} \\
 \text{,, No. 4.} & \quad \frac{17 \times 1.4}{0.08} \text{ ,,} = 298.0 \text{ ,,}
 \end{aligned}$$

Inasmuch as the value of the term CR is always small compared with E, in the expression $e = E - CR$, a much greater

error in the determination of R than that included in the above estimates will produce no material effect on the accuracy of the determination of e .

Voltmeter No. 1.

Surface of each electrode = 27.5 square centimetres.

Mean Current, in microwebers.	Microwebers per square centim. of electrode surface.	Average value of E , in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
1.6	0.06	1.480	1.480	No visible evolution of gas.
3.1	0.11	1.622	1.622	" "
8.5	0.31	1.878	1.878	Distinct evolution of gas.
11.2	0.41	1.897	1.897	" "
25.1	0.91	1.971	1.971	" "
62.8	2.28	2.062	.001	2.061	" "
119.4	4.34	2.129	.001	2.128	" "
216.7	7.88	2.218	.003	2.215	" "
310.0	11.3	2.274	.004	2.270	" "
543.7	19.8	2.333	.007	2.326	" "

Voltmeter No. 2.

Surface of each electrode = 8.0 square centimetres.

Mean Current, in microwebers.	Microwebers per square centim. of electrode surface.	Average value of E , in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
4.6	0.57	1.899	1.899	No visible gas evolved.
11.5	1.42	2.012	2.012	Gas visibly evolved.
31.2	3.90	2.107	2.107	" "
52.0	6.55	2.170	.001	2.169	" "
97.2	12.15	2.245	.001	2.244	" "
141.6	17.7	2.302	.002	2.300	" "
250.1	31.3	2.371	.003	2.368	" "
508.0	63.5	2.468	.006	2.462	" "
866.0	109.3	2.522	.010	2.512	" "

Voltmeter No. 3.

Surface of each electrode = 3.2 square centimetres.

Mean Current, in microwebers.	Microwebers per square centim. of electrode surface.	Average value of E , in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
0.12	0.03	0.892	0.892	No gas evolved.
4.3	1.34	1.700	1.700	" "
6.4	2.00	1.996	1.996	Slight evolution of gas.
10.3	3.2	2.086	2.086	Gas visibly evolved
12.8	4.0	2.153	2.153	" "
20.6	6.4	2.183	2.183	" "
29.0	9.1	2.231	2.231	" "
53.8	16.8	2.303	2.303	" "
99.0	30.9	2.368	.001	2.367	" "
211.0	65.9	2.415	.002	2.413	" "
384.0	120.0	2.468	.003	2.465	" "

Voltameter No. 4.

Surface of each electrode = 0.19 square centimetre.

Mean Current, in microwebers.	Microwebers per square centim. of electrode surface.	Average value of E , in volts.	CR, in volts.	$e = E - CR$, in volts.	Remarks.
0.34	1.8	1.484	1.484	No gas evolved.
0.9	4.7	2.032	2.032	" "
1.2	6.3	2.069	2.069	" "
2.8	14.7	2.275	.001	2.274	Slight evolution of gas.
3.4	17.8	2.291	.001	2.290	Distinct evolution of gas.
4.8	25.2	2.336	.001	2.335	" "
6.1	32.1	2.367	.002	2.365	" "
8.9	46.8	2.410	.003	2.407	" "
16.6	87.4	2.496	.005	2.491	" "
36.1	190.0	2.578	.011	2.567	" "
67.1	353.0	2.629	.020	2.609	" "
145.0	763.0	2.702	.044	2.658	" "
248.0	1305.0	2.753	.074	2.679	" "

88. Figs. 2 and 3 represent the curves thus obtained, the curves numbered 1, 2, 3, and 4 being those respectively obtained with the voltameters thus numbered; in fig. 2 the currents are plotted as abscissæ, and the values of e as ordinates. Evidently, from the nature of these curves, the following conclusions may be drawn:—

- (1) As the current increases with a given voltameter the value of e increases, but at a less rapid rate; so that the curves are concave downwards.
- (2) For a given current the value of e is the greater the smaller the electrode surface.

In fig. 3 the abscissæ are the quantities of electricity flowing per second per square centimetre of electrode surface*; evidently the four curves obtained with the four voltameters do not differ more from one another than may reasonably be ascribed to the not absolute uniformity of the conditions of

* Those determinations in which no hydrogen was evolved are omitted in every case, inasmuch as the effects of diffusion discharge are unequal for the different voltameters, and hence unequally reduce the value of e , leading to marked difference in the curves.

the surface of the electrodes (Nos. 1 and 2 being chiefly foil, No. 3 partly foil partly wire, and No. 4 wholly platinum wire), and to the unavoidable experimental errors; whence it may be concluded that

- (3) for a given rate of flow of electricity per unit area of electrode, the value of e is independent of the size of the electrodes and of the current passing; *i. e.*, e remains the same when both electrode surface and current are altered in the same ratio.

Effect of Variation in the Strength of the dilute Acid used.

89. It has been concluded by previous experimenters that increasing or decreasing the strength of the dilute sulphuric acid electrolysed makes little or no difference in the value of e , and that, if any difference exist, it is in this direction—that the stronger acid gives, *ceteris paribus*, a smaller value for e , the effect being less nearly imperceptible with very weak solutions indeed, and being well marked when distilled water is compared with weak acid. The following experiments were made with the above-described voltameters, from which it results that as the strength of the acid is increased (from 0.2 to 40.0 grammes per 100 cubic centims.) a progressive diminution in the value of e ensues.

Acid containing 40.0 grammes of H_2SO_4 per 100 cubic centims.—Voltmeter No. 1 was used: from Kohlrausch's numbers (Pogg. Ann. Ergbd. viii. p. 1, and clix. p. 233) it results that acid of 1.2207 sp. gr. containing 30 per cent. of H_2S_4O , and therefore containing in 100 cubic centims. 36.6 grammes of H_2SO_4 , has a specific resistance of 1.37 ohm at 18° , whilst acid of sp. gr. 1.2625, containing 35 per cent., or 44.2 grammes per 100 cubic centims., has the specific resistance 1.40 ohm at 18° ; whence evidently the specific resistance of acid of 40 grammes per 100 cubic centims. strength may be taken as 1.385 ohm at 18° , or close to 1.4 ohm, nearly the same as for acid of strength equal to 27.0 grammes per 100 cubic centims. (the minimum specific resistance being known to be at strength intermediate between 30 and 35 grammes per 100 cubic centims.); so that R is, as before, close to 12.1 ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR.$
3.1	0.11	1.564	...	1.564
4.0	0.14	1.663	...	1.663
5.5	0.20	1.761	...	1.761
8.6	0.31	1.801	...	1.801
13.6	0.49	1.843	...	1.843
21.2	0.77	1.891	...	1.891
47.1	1.71	1.972	.001	1.971
76.3	2.77	2.034	.001	2.033
204.0	7.42	2.105	.002	2.103
281.0	10.2	2.143	.003	2.140
370.0	13.4	2.181	.005	2.176
679.0	24.7	2.223	.008	2.215
1140.0	41.4	2.303	.014	2.289

Acid containing 11.4 grammes of H_2SO_4 per 100 cubic centims.—Voltmeter No. 3 employed. Value of R calculated from Kohlrausch's determination of sp. resistance* of sulphuric acid = $\frac{6 \times 2.5}{1.1} = 13.6$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e = E - CR.$
6.8	2.1	2.125	...	2.125
9.8	3.1	2.156	...	2.156
12.3	4.0	2.218	...	2.218
16.9	5.3	2.256	...	2.256
29.0	9.0	2.297	...	2.297
45.8	14.3	2.340	.001	2.339
70.1	21.9	2.362	.001	2.361
109.9	34.4	2.420	.002	2.418
212.0	66.2	2.486	.003	2.483
306.6	94.8	2.529	.004	2.525

By interpolation from these values it is rendered evident that whilst with acid of 40 grammes per 100 cubic centims. the values of e for given currents were uniformly lower than those for the same currents obtained with the same voltmeter and acid of 27.0 grammes per 100 cubic centims., the reverse holds with acid of 11.4 grammes per 100 cubic centims. The fol-

* Acid of 1.0673 sp. gravity containing 10 per cent. H_2SO_4 , corresponding to 10.7 grammes per 100 cubic centims., gives sp. resistance at $18^\circ = 2.59$ ohms; and acid of sp. gr. 1.1036 containing 15 per cent., corresponding to 16.6 grammes per 100 cubic centims., gives sp. resistance 1.87 ohm; whence, by interpolation, acid of 11.4 grammes per 100 cubic centims. has sp. resistance 2.50 ohms.

lowing figures show that this is *à fortiori* true for acid of 1.0 and of 0.192 gramme per 100 cubic centims.

Acid containing 1.0 gramme H_2SO_4 per 100 cubic centims.—
 Voltmeter No. 2 used. Value of specific resistance of acid of 1 per cent. or sensibly 1 gramme per 100 cubic centims.,
 22.1 (Kohlrausch), whence $R = \frac{8 \times 22.1}{1.0} = 177$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e = E - CR.$
3.7	0.46	1.939	.001	1.938
10.0	1.25	2.165	.002	2.163
36.0	4.5	2.285	.007	2.278
124.0	15.5	2.415	.022	2.393
291.0	36.4	2.495	.052	2.443
363.0	45.4	2.527	.064	2.463
498.0	62.2	2.607	.088	2.519
754.0	94.2	2.751	.133	2.618

Voltmeter No. 1 used. Value of $R = \frac{13 \times 22.1}{1.5} = 192$ ohms.

Current.	Microwebers per square centimetre.	E.	CR.	$e = E - CR.$
7.8	0.28	1.993	.002	1.991
17.3	0.63	2.114	.003	2.111
27.2	0.99	2.141	.005	2.136
48.1	1.75	2.193	.009	2.184
88.7	3.23	2.253	.017	2.236
149.3	5.43	2.294	.029	2.265
324.3	11.8	2.387	.063	2.324
442.0	16.1	2.431	.085	2.346

Just as with acid of 27.0 grammes per 100 cubic centims. (§ 91 and 92), the two curves obtained with acid of 1 gramme per 100 cubic centims. with voltmeters Nos. 1 and 2 are sensibly identical.

Acid containing 0.192 gramme per 100 cubic centims.—Kohlrausch and Nippoldt found that the resistance of acid of 0.2 per cent. H_2SO_4 was 465100 times that of mercury at 22°, whence the specific resistance of acid of .192 gramme per 100 cubic centims. may be taken as close to 45 ohms; so that with the voltmeter used $R = \frac{6 \times 45}{1.1} = 245$ ohms, the plates being 6 centimetres apart, and the bore of the tube between them

averaging 1.1 square centimetre in section. The surface of each electrode with this voltameter was 3.5 square centimetres.

Current.	Microwebers per square centimetre.	E.	CR.	$e = E - CR.$
4.6	1.31	2.186	.001	2.185
15.2	4.84	2.300	.004	2.296
31.7	9.1	2.363	.008	2.351
60.3	17.2	2.468	.015	2.453.
100.9	28.8	2.542	.025	2.517

Fig. 4 represents the curves obtained with these different strengths of acid, the abscissæ being in each case the current-flow per square centimetre of electrode surface: curve no. 1 is that obtained with acid of 40.0 grammes per 100 cubic centims.; the curve marked no. 2, that with acid of 11.4 grammes; those marked 3a and 3b the two with acid of 1.0 gramme per 100 cubic centims., obtained respectively with voltameters no. 2 and no 1; the curve marked 4 is that with acid of 0.192 gramme per 100 cubic centims.; whilst curve no. 5 is the average curve deduced for acid of 27.0 grammes per 100 cubic centims. from the preceding four sets of experiments. In all cases, *the weaker the acid the greater is the counter E.M.F. set up with a given rate of flow of electricity per unit area of electrode surface.*

Effect of Variation of the Material of the Electrode.

90. It is well known, from the experiments of previous observers, that the nature of the surface of the electrode considerably affects the value of the counter E.M.F. set up, and that in particular platinizing a platinum electrode largely decreases the counter E.M.F. set up by a given current. This effect, however, is partly due to the considerable increase in effective surface thereby occasioned. In order to see what effects would be produced by substituting polished gold or compact carbon for polished platinum, the following experiments were made:—The carbon electrodes were thin slabs about 1–2 millimetres thick, sawn from hard rods used for electric lights; they were were filed to a tolerably smooth

surface, and digested for some months with aqua regia—also boiled at intervals with hydrochloric, nitric, and dilute sulphuric acids. To make connection with the battery, the upper portions were wrapped round with platinum foil tightly tied on with platinum wire, connected to the glass mercury-cup supporting the electrodes; the whole of the platinum foil and wire was then covered with gutta percha, so that only carbon was exposed to the liquid in the voltameter. To make sure that as little as possible of metals &c. capable of being acted on by nascent electrolytic oxygen was present, they were used as + electrodes for several days in the electrolysis of dilute H_2SO_4 , such a current being employed as to keep a continuous evolution of gas at the rate of some 50 to 100 cubic centims. of hydrogen per day. The superficial area of each electrode (measured by scale and compasses, and making no allowance for increase of surface due to the carbon being slightly pitted and not smooth) was 3.9 square centimetres.

The gold electrodes were similarly mounted, a platinum wire being fused to them, and the surface of the platinum covered with gutta percha, so that only gold was exposed to the liquid in the voltameter. Surface of each electrode = 17.0 square centimetres.

Values obtained with Acid containing 27 grammes per 100 cubic centims.

Gold Electrodes.

The distance apart of the centres of the electrodes was 15 centimetres, and the bore of the tube between them 1.1 square centimetre; so that $R = \frac{15 \times 1.4}{1.1} = 19.1$ ohms.

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR.$
9.8	0.58	2.139	...	2.139
14.7	0.86	2.312	...	2.312
34.0	2.00	2.407	.001	2.406
55.7	3.27	2.452	.001	2.451
156.9	9.23	2.515	.003	2.512
364.0	21.4	2.627	.007	2.620
668.6	39.3	2.701	.013	2.688

Carbon Electrodes.

The distance apart of the centres of the electrodes was 18 centimetres, and the bore of the tube 1·5 square centimetre; so that

$$R = \frac{18 \times 1.4}{1.5} = 16.8 \text{ ohms.}$$

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR.$
6.7	1.7	1.446	...	1.446
8.1	2.1	1.460	...	1.460
10.9	2.7	1.504	...	1.504
16.7	4.3	1.583	...	1.583
32.2	8.3	1.662	.001	1.661
103.3	26.5	1.761	.002	1.759
135.8	34.8	1.782	.002	1.780
238.0	61.0	1.829	.004	1.825

Values obtained with Acid containing 1 gramme of H_2SO_4 per 100 cubic centims.

Gold Electrodes.

$$R \text{ in this case} = \frac{15.0 \times 22.1}{1.1} = 301 \text{ ohms.}$$

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR.$
7.9	0.46	2.211	.002	2.209
27.8	1.63	2.401	.008	2.393
68.1	4.01	2.483	.020	2.463
130.0	7.65	2.562	.039	2.523
238.0	16.9	2.659	.086	2.573
496.0	29.2	2.775	.149	2.626

Carbon Electrodes.

$$R \text{ now} = \frac{18.0 \times 22.1}{1.5} = 265 \text{ ohms.}$$

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR.$
5.6	1.4	1.500	.001	1.499
13.7	3.5	1.614	.004	1.610
25.2	6.4	1.701	.007	1.694
55.4	14.2	1.763	.015	1.748
85.1	21.8	1.823	.023	1.800
248.0	63.5	1.938	.067	1.871

Fig. 5 (Pl. VI.) represents the four curves thus obtained,—those marked 1 and 3 being the curves obtained with acid of 27·0 grammes per 100 cubic centims., and with carbon and gold electrodes respectively; and those marked 4 and 6 the curves obtained with acid of 1·0 gramme per 100 cubic centims., with carbon and gold electrodes respectively. The other two curves traced, marked 2 and 5, are put in for comparison, being respectively the mean curves obtained as above described with acid of 27·0 and 1·0 grammes per 100 cubic centims. with platinum electrodes. In each case the weaker acid gives the higher counter E.M.F. for a given rate of flow of electricity per square centimetre of electrode surface; but the effect produced by the variation in the strength of the acid is small compared with that produced by substituting platinum for carbon, or gold for platinum*.

It should be noticed, however, that it is highly probable that the counter E.M.F. observed with the carbon electrodes is somewhat diminished, at any rate for the smaller currents, by the circumstance that electrolytic “nascent” oxygen is capable of attacking carbon, forming CO and CO₂ (Beetz, *Wied. Annalen*, 1878 [2] v. p. 1; also *Phil. Mag.* 1879 [5] vii. p. 1); the effect of this would of course be to diminish e by a quantity equivalent to the heat evolved in the oxidation of the carbon (reckoned per gramme-equivalent of water decomposed). With currents of the minuteness of only a few microwebers it was not found practicable to prove directly the formation either of CO or CO₂; but the circumstance that the observed values for e fell slightly below 1·50 volt with the voltameter containing acid of 27 grammes per 100 cubic centims., and with currents of from 5 to 10 microwebers, or slightly above the current equivalent to the “diffusion discharge” found with the same voltameter substituting platinum electrodes for carbon ones (viz. close to 4·0 microwebers), together with the circumstance that with platinum and gold electrodes the value of e was never below 1·5 volt when the

* The two carbon curves lie a little below their true positions, owing to the effective area of the carbons being a little greater than their superficial measurement, on account of the unavoidable absence of perfect smoothness and slight pitting of the surface. The true area, however, exceeds that measured by only a small amount, the carbon surface having been filed and ground so that the surface was as nearly smooth as it could be made.

current exceeded that equivalent to the "diffusion discharge," would seem to indicate that the values of e for these currents found for the carbon electrodes were actually slightly below the values that would have been found had no oxidation of the electrode taken place.

Experiments with Oxidizable Electrodes.

91. Suppose that dilute sulphuric acid is electrolysed with copper electrodes so that a gramme-equivalent of copper sulphate is formed at the + electrode for one of hydrogen evolved at the - electrode. In accordance with the general theorem (§ 61),

$$e = E_1 + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J,$$

the value of e will be

$$e = E_1 + \{(1-n_1)H_1 - n_1h_1 - H_3\}\chi J,$$

where H_3 is the heat evolved during the production of a gramme-equivalent of copper sulphate from copper, ordinary free oxygen, and dilute sulphuric acid; for in this case $\Sigma(H)$ is equal to $H_3 + (1-n_2)H_2 - n_2h_2$ (the n_2 , h_2 , and H_2 referring to oxygen, and n_1 , h_1 , and H_1 to hydrogen), the diffusion effect of the copper sulphate solution accumulating round the + electrode being left out of sight.

Writing E_3 for $H_3\chi J$,

$$e = E_1 - E_3 + \{(1-n_1)H_1 - n_1h_1\}\chi J.$$

Of course, if some other metal be used instead of copper, *e. g.* zinc, the same formula will apply, only the value of E_3 will be different.

If, instead of dilute sulphuric acid, a metallic salt, *e. g.* zinc or copper sulphate, be electrolysed, the same formula will hold, E_1 now representing the E.M.F. corresponding to the work done in decomposing the salt electrolysed into oxygen, metal, and dilute sulphuric acid, and E_3 , as before, being the E.M.F. representing the work gained in synthesizing the salt produced by the solution of the + electrode from metal, oxygen, and dilute sulphuric acid; since $h_1=0$ when a solid metal is produced,

$$e = E_1 - E_3 + (1-n_1)H_1\chi J.$$

Taking into account the diffusive effect due to the strengthening of the metallic salt-solution round the + electrode and

its weakening round the — electrode [which, according to the results of Moser (Wied. *Annalen*, iii. p. 216), H. F. Weber (Phil. Mag. [5] viii. pp. 487 and 523), and Helmholtz (Wied. *Annalen*, iii. p. 201), may amount to at least some few hundredths of a volt under certain circumstances], this formula becomes

$$e = E_1 - E_3 + \{(1 - n_1)H_1 + h'\}\chi J,$$

where h' is the heat corresponding to the diffusive effect of the concentrated and weak solutions per gramme-equivalent of electrolyte decomposed; h' is of + sign, since the results of the above experimenters show that the effect of the different densities of the solutions round the two electrodes is to cause a current to flow through the fluid from the weaker to the stronger solution, *i. e.* from the — to the + electrode*, or in the opposite direction to the current producing electrolysis.

If, then, dilute sulphuric acid, for instance, be decomposed by means of oxidizable electrodes, say of copper, the value of e will, under any given condition, be given by the formula

$$e = \{h' + h'' + (1 - n_1)H_1 - n_1h_1\}\chi J,$$

where $h''\chi J = E_1 - E_3$.

The same formula will also apply when a metallic salt is decomposed, $h''\chi J$ still representing $E_1 - E_3$, whatever values these two quantities may happen to possess. If the metallic salt decomposed contain the same metal as that dissolved from the + electrode, E_1 will approximately = E_3 , and h'' will nearly = 0. Since, however, the physical condition of the deposited and dissolved metal will rarely, if ever, be identical, E_1 will not exactly = E_3 ; h'' will represent the heat that would be evolved in the transformation of a gramme-equivalent of deposited metal into the physical condition of the dissolved electrode.

Since $h_1 = 0$ when a solid is deposited, the formula simplifies to this,

$$e = \{h' + h'' + (1 - n_1)H_1\}\chi J.$$

* Presumably this is only the case when heat is *developed* by the mixture of the strong and weak solutions; were heat *absorbed* during the intermixture, probably the current would be reversed in direction; for in that case the expenditure of work in order to effect electrolysis would be less instead of greater when the strong and weak solutions accumulated round the electrodes than it would be did diffusion and intermixture take place instantaneously.

So-called non-polarizable electrodes are, strictly speaking, misnomers ; they are only cases where the value of e is very small, owing to the particular conditions of the experiment rendering $(1-n_1)H_1 + h' + h''$ but little greater than 0.

If the value of n_1 decreases as the current increases, when it refers to a metal deposited, as appears to be the case when it refers to hydrogen, from the above described experiments it results that the value of e will continually increase with the current, if the conditions of the experiment are such that h' and h'' remain constant (or if they are negligible).

92. *Decomposition of Acidulated Water with Copper Electrodes.*—In order to examine these points experimentally, known currents were passed through a U-voltmeter filled with well-boiled, just cooled, dilute sulphuric acid containing 11.5 grammes of H_2SO_4 per 100 cubic centims., and fitted with copper electrodes each exposing a surface of 8.5 square centimetres. After allowing a current of some 50 to 100 microwebers to pass for two or three days the values of e became approximately steady ; the following numbers were obtained, the electrodes being 13 centimetres apart and the bore of the U-tube between them 1.09 square centimetre, so that the value of $R = \frac{13 \times 2.5}{1.09} = 30$ ohms, 2.5 ohms being (as calculated in § 89, footnote) the specific resistance of sulphuric acid of 11.4 grammes per 100 cubic centims. The values of E are all probably a little underestimated, because it was found impossible to allow a current of 25 to 50 microwebers to pass for a fortnight, so as completely to saturate the acid round the — electrode and the electrode itself with hydrogen, and get rid of the last traces of dissolved oxygen, as was done with platinum, carbon, or gold electrodes ; for before a fortnight had elapsed, the copper dissolved from the + electrode and converted into copper sulphate had diffused to the other electrode and became partly re-deposited there (at least this phenomenon was observable in less than a fortnight when a polished platinum plate was used instead of a copper one for the — electrode). Probably this source of error affects all the observations about equally, and is but slight, since sensibly the same values of E were observed for a given current whether the observations were made on the 4th or on the 9th day.

Current, in microwebers.	Microweber per square centi- metre of elec- trode surface.	E, in volts.	CR.	$e = E - CR.$
9.7	1.14	.523523
20.1	2.34	.548	.001	.547
49.8	4.23	.586	.001	.585
77.1	9.06	.600	.002	.598
103.7	12.4	.616	.003	.613
174.7	20.5	.669	.005	.664
226.0	26.6	.685	.007	.678
378.0	44.5	.720	.011	.709

These numbers clearly show that the values of $h' + (1 - n_1)H_1 - n_1h_1$ for currents of not less than 1.14 microweber per square centimetre of electrode surface are positive, and increase as the current increases; for h'' cannot exceed 0.4 volt, and the sum of h'' and $h' + (1 - n_1)H_1 - n_1h_1$ is uniformly greater than this. [That h'' is not > 0.4 volt results from the valuations of E_3 cited in Part I. § 21 and 22, deduced from the experiments of Favre, Julius Thomsen, and Raoult, which varied between 1.162 and 1.321, being uniformly above 1.1 volt, so that, as $E_1 = 1.50$ volt (Part II.), $h'' = E_1 - E_3$ cannot exceed 0.4 volt.] This increase is mainly due to the decrease in value of n_1 as the current increases; for on altering the current-strength to some value previously experimented with, the value of e always immediately altered to something very close to the value it previously was found to possess for the altered current, which could not have been the case had the increase in value of e found for a stronger current been simply due to the increase in the value of h' owing to the accumulation of copper sulphate solution round the + electrode.

Very little difference in the value of E was noticed when gold was substituted for copper as the negative electrode (the dimensions and the positive electrode remaining unchanged), the curve deduced by plotting the values of $E - CR$ as ordinates and the rates of flow per square centimetre as abscissæ being nearly, though not quite, the same whether the — plate were copper or gold; what little difference did exist was of such a nature that the gold — electrode curve lay slightly above the copper one. On substituting platinum for

copper, the curve was very distinctly depressed; *i. e.* the values of $E - CR$ for a given rate of flow and a constant copper positive electrode were smaller with a platinum electrode than with a copper one, and smaller with a copper one than with a gold one. Whether the values thus registered by the aid of the quadrant-electrometer are strictly comparable, or whether they are complicated by a difference of contact action taking place between the electrode and the brass quadrant of the electrometer (by means of the connecting-wire), is, however, open to discussion *. Admitting that the contact action does not materially affect the values obtained, the numbers found with the gold, copper, and platinum — electrodes would indicate that the value of n_1 is greater with platinum than with copper and greater with copper than with gold; *i. e.* the “condensing” actions of the three metals for “nascent” hydrogen lie in the order, platinum greatest, then copper, and lastly gold. As regards platinum and gold, this is precisely the conclusion to be drawn from the experiments described in § 90.

Experiments bearing further on the phenomena observed when the electrodes are not of the same material, will be considered in a future paper.

93. *Decomposition of Copper Sulphate with Copper Electrodes, and of Zinc Sulphate with Zinc Electrodes.*—The voltmeters used consisted simply of U-tubes filled with the hot, just boiled, solution of zinc or copper sulphate employed, and then closed by india-rubber stoppers through which passed glass tubes with platinum wires through the drawn-out ends, so as to make mercury-cups, and keep the solution from access

* It is manifest that, whatever may be the nature of the contact actions between two dissimilar metals &c., and however this may affect the determination of the true difference of potential between two dissimilar plates connected respectively with the two quadrants of an electrometer, such actions have no influence at all on the result when the two metals are the same; so that whilst the mercury in a mercury-cup and two thick copper wires dipping into it may differ in potential, yet the two wires will be at the same potential, *i. e.* just away from the mercurial surface; and the difference of potential between the two quadrants of an electrometer is the same as that between the two plates of a voltmeter &c. respectively connected with them when these plates are of the same material, *e. g.* platinum, although the intermediate connecting-wires and plates themselves may differ in their absolute potentials from the quadrant-potentials.

of air; to the platinum wires were soldered the electrodes, consisting of well-brightened strips of metal of known size, the solderings and platinum wire being covered over with gutta percha. By introducing a known resistance into the circuit, composed of voltameter and electromotor (one or more De la Rue, or other analogous cells), the current could be regulated and measured, and hence the value of $e = E - CR$ determined. In this way the following numbers were obtained. With the copper-sulphate voltameter (which contained a nearly saturated solution of the salt, containing 7.84 grammes metallic copper per 100 cubic centims., the formula $\text{CuSO}_4 \cdot 36\text{H}_2\text{O}$ requiring 7.80) the value of R was found to be close to 110 ohms at the average temperature of the observations—this number being calculated from the dimensions of the column of fluid between the electrodes, and the specific resistance of the fluid determined by a new method which will be described in detail in a future paper. Similarly, the value of R for the zinc-sulphate voltameter was calculated to be close to 250 ohms.

The following numbers were obtained with copper-sulphate and copper electrodes :—

Surface of each electrode = 8.65 square centimetres.

(I.) *Values obtained when each electrode was new, i. e. polished compact rolled copper plate.*

Current, in microwebers.	Microwebers per square centimetre of electrode surface.	E, in volts.	CR.	$e = E - CR$.
7.1	0.8	.032	.001	.031
14.6	1.7	.033	.002	.031
23.8	2.7	.036	.003	.033
30.8	3.6	.036	.003	.033
35.7	4.1	.039	.004	.035
73.0	8.4	.047	.008	.039
148.0	17.1	.060	.016	.044
185.8	21.5	.062	.020	.042
247.0	28.6	.073	.027	.046
371.0	42.9	.088	.041	.047
728.0	84.2	.131	.080	.051

(II.) *Values obtained with electro-deposited copper on each electrode.*

(a) When the copper had been deposited some 48 hours, the electrodes being in the voltameter out of contact of air:—

15.2	1.7	.018	.002	.016
30.2	3.5	.025	.003	.022
91.5	10.6	.036	.010	.026
212.0	24.7	.050	.023	.027
403.0	46.6	.079	.044	.035
749.0	86.6	.137	.082	.055

(b) When the copper had not been deposited so long, from 15 to 20 hours after deposition:—

15.2	1.7	.015	.002	.013
22.8	2.6	.017	.003	.014
30.2	3.5	.020	.003	.017
45.0	5.2	.024	.005	.019
89.1	10.3	.033	.010	.023
253.0	29.2	.052	.028	.024
420.0	48.6	.078	.046	.032
774.0	89.6	.130	.085	.045
1328.0	153.5	.205	.146	.059

(c) When the copper had only been deposited a few minutes before each observation was made:—

16.6	1.9	.011	.002	.009
28.4	3.3	.014	.003	.011
42.3	4.9	.018	.005	.013
134.5	15.5	.031	.015	.016
240.0	27.7	.048	.026	.022
383.0	44.3	.070	.042	.026
740.0	85.5	.116	.081	.035
1311.0	151.6	.190	.144	.046

By interpolation, the following values for e are calculated from the above figures:—

Current, in microwebers.	I.	IIa.	IIb.	IIc.
10	.031	—	—	—
20	.032	.017	.014	.010
50	.037	.023	.020	.013
100	.041	.026	.023	.015
200	.043	.027	.024	.020
500	.049	.043	.036	.029
1000	—	—	.050	.040

From which it is evident that the more freshly deposited the electro-copper was, the less was the value of e ,—leading to the conclusion that either the freshly deposited copper had a higher power of “condensing” copper on its surface than rolled copper, thereby increasing the value of n_1 in the formula

$$e = \{h' + (1 - n_1)H_1 + h''\} \chi J,$$

and that this power became lessened on standing, or else that, on standing, the surface of the copper altered in such a way as to cause the value of h'' to increase, or, possibly, that both changes took place together.

Precisely analogous results were obtained in other experiments with different voltmeters: with considerably stronger currents up to some 5000 microwebers per square centimetre of electrode surface, values of 0·2 volt and upwards have been obtained for e by a method now being elaborated in conjunction with Mr. E. H. Rennie. Admitting that in these instances the values of h' and h'' are negligible compared with $(1 - n_1)H_1$ (which probably is not quite the case), it results that the value of $H_1 \chi J$ must exceed 0·2 volt, *i. e.* that H_1 , the heat of transformation of “nascent” into ordinary copper, is greater than $0 \cdot 2 \times 10^8$
 $\frac{4410}{4410} = 4500$ gramme-degrees per gramme-equivalent.

94. In precisely the same way the following values were obtained on electrolysing a solution of zinc sulphate with bright zinc electrodes, the area of each of which was 8·6 square centims., the value of R being close to 250 ohms.

Current, in microwebers.	Microwebers per square centim. of electrode surface.	E, in volts.	CR.	$e = E - CR.$
14·3	1·7	·023	·004	·019
28·2	3·3	·031	·007	·024
39·4	4·6	·039	·010	·029
69·8	8·1	·050	·017	·033
87·9	10·2	·068	·022	·046
136·4	15·9	·085	·034	·051
167·1	19·4	·094	·042	·052
310·0	36·0	·131	·078	·053
647·0	75·2	·232	·162	·070
1147·0	132·5	·365	·287	·078

The curves traced out with zinc- and copper-sulphate solutions and zinc and copper poles respectively exhibit resemblance in general characters to those obtained with acidulated water and non-oxidizable electrodes: they indicate that e increases with the current but not so rapidly, so that the curves are concave downward.

95. Under certain conditions, the value of h'' in the formulæ arrived at in § 91, representing the counter E.M.F. set up during electrolysis, may become negative, but numerically greater than $h' + (1 - n_1)H_1 - n_1h_1$. In such a case negative work must be spent (or work will be gained) during the decomposition; the cell is then termed an electromotor, and constitutes an ordinary galvanic element. When this is the case, $E_3 > E_1$,—as, for instance, when the + electrode is zinc and dilute sulphuric acid is electrolysed, or when copper sulphate is electrolysed as a partitioned cell, the one half containing zinc sulphate with a plate of zinc therein constituting the + electrode (Daniell's cell). The previous experiments show that the value of the expressions

$$h' + (1 - n_1)H_1 - n_1h_1 \quad \text{and} \quad h' + (1 - n_1)H_1$$

(according as a gas or a solid is evolved at the negative electrode) are positive even with very small currents, and increase as the current increases. It hence results that the numerical value of the negative counter E.M.F. set up in a simple voltaic circuit of zinc, another metal, and dilute sulphuric acid, or in a Daniell's cell (*i. e.* the actual E.M.F. of the cell*), must decrease as the current produced by it increases.

* The E.M.F. of an electromotor is defined for the present purpose as the difference of potential set up between two poles of the same material (*e. g.* the two brass quadrants of an electrometer, or two copper conducting-wires, the one connected with one plate of the electromotor, the other with the other) corrected for the effect of the current passing (if appreciable) due to the external resistance. Whatever may be the influence of contact actions upon this corrected potential-difference in any given case, this influence must be constant for a given apparatus, and independent of the current generated, so that any change in the potential-difference set up is not due in any way to contact-action between the metallic plates and conducting-wires &c. The correction is of this form:—Let E_1 be the actual difference of potential and E_2 the E.M.F. of the electromotor, let R_1 be the external resistance and R_2 the resistance of the electromotor, and let C be the current passing (which = 0 if R_1 is indefinitely great); then

In the case of a simple voltaic circuit, this effect is wholly distinct from one often observed in a newly set-up cell charged with dilute acid containing dissolved air. When first set to work the action of the cell is greatly intensified by the oxidation of the evolved hydrogen by the dissolved oxygen (much as is the case in a Leclanché element, the oxygen coming from the manganese dioxide); but by-and-by this ceases and the E.M.F. goes down. This effect is often said, vaguely and not strictly correctly, to be due to the plates becoming "polarized" by hydrogen, the which phrase really applies to the wholly different phenomenon now under consideration.

That the E.M.F. of a Daniell cell is somewhat less when generating a current than when no current passes has already been shown to be the case by Waltenhofen (*Sitzb. Akad. Wien*, xlix. 2, p. 229) and by Beetz, using a modification of the method of compensation (*Pogg. Ann.* cxlii. p. 581, 1871). Apparently, however, physicists generally are under the impression that the diminution in E.M.F., or "polarization" of the cell, thus produced is practically inappreciable: thus, for instance, within the last few months a determination of the value of v has been made in Sir W. Thomson's laboratory by R. Shida, by measuring the E.M.F. of a gravity Daniell, first, in electrostatic units (no current being generated), and then in electromagnetic units (a moderately powerful current being set up); the which method evidently can only be applied if the difference in the E.M.F. according as a current is generated or not is negligible (*Brit. Assoc. Reports*, 1880, p. 497). The same kind of remark applies to several other investigations published during the last few years.

96. *Decomposition of Dilute Sulphuric Acid with a Zinc Positive Electrode.*—On trying experiments with a zinc (amalgamated) positive electrode and a platinum electrode in the same way as those described in § 92, it was found that the numerical value of e was uniformly negative and decreased as the cur-

$E_2 = \frac{R_1 + R_2}{R_1} E_1$, $E_1 = E_1 + CR_2$. For the total work done by the current in a time t is $C^2(R_1 + R_2)t$, which $= E_2 Ct$, whilst the work done outside the electromotor is $C^2 R_1 t = E_1 Ct$; whence

$$E_2 = E_1 \times \frac{R_1 + R_2}{R_1} = E_1 + R_2 \times \frac{E_1}{R_1} = E_1 + CR_2.$$

rent increased. So long as the current remained of a constant value the nature and dimensions of the external battery were immaterial; so that *the same value for e was obtained whether an external battery was actually applied, or whether the zinc-platinum couple was the sole electromotor in circuit*, provided that, by suitably adjusting the total resistance in circuit, the current was made the same. Thus the following average numbers were obtained with a cell containing dilute sulphuric acid of 10 grammes H_2SO_4 per 100 cubic centims., the plates each exposing 8.6 square centims. of surface, and being contained in a U-voltameter like those above described, of 1.1 square centim. bore, the centres of the plates being 13 centims. apart; so that, as the specific resistance of sulphuric acid of the strength used is close to 2.9 ohms at 18° (from Kohlrausch's numbers, *loc. cit. supra*), the value of R was close to $\frac{13 \times 2.9}{1.1} = 34$ ohms:—

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e = -(E - CR)$.
6.7	0.78	-.604604
9.8	1.14	-.589589
14.4	1.67	-.571571
23.2	2.7	-.547	.001	.548
41.0	4.8	-.519	.001	.520
58.5	6.8	-.493	.002	.495
96.0	11.2	-.442	.003	.445
135.6	15.8	-.395	.005	.400

Evidently the value of $-(E - CR)$ —that is, the direct E.M.F. of the combination—decreases as the current increases, but not at the same rate, the diminution in the E.M.F. being less rapid than the increase in rate of flow.

97. *Daniell's Cell*.—In order to verify the deductions above made from the preceding experiments as to the variation of the E.M.F. of a Daniell's cell with the current produced, and so to amplify the observations of Waltenhofen and Beetz, the following experiments were made with two such cells arranged on the "gravity" principle—*i. e.* no porous cell being employed, but the copper plate being lowest and immersed in a saturated solution of copper sulphate, the zinc plate being uppermost and immersed in a solution of zinc sulphate of

lower specific gravity than the copper sulphate solution. In the first cell the active surface of each plate was about 15 square centims., and the resistance of the column of fluid between them was calculated, from the dimensions of the column and Kohlrausch's values for the specific resistances of copper and zinc sulphate solutions, to be about 4 ohms. In the second cell much smaller plates were used, exposing about 1 square centim. of active surface, the resistance of the column of fluid being calculated to be about 40 ohms.

First Cell.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e = -(E - CR).$
0	0	-1.090	...	1.090
10.9	0.7	-1.090	...	1.090
36.3	2.4	-1.090	...	1.090
107.7	7.2	-1.077	...	1.077
267.2	17.8	-1.069	.001	1.070
530.5	35.4	-1.061	.002	1.063
1317.5	87.8	-1.054	.005	1.059

Second Cell.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e = -(E - CR).$
0	0	-1.105	...	1.105
11.2	11	-1.105	...	1.105
36.8	37	-1.094	.001	1.095
109.1	109	-1.082	.004	1.086
265.5	266	-1.053	.010	1.063
515.5	516	-1.020	.021	1.041
1140.0	1140	-0.982	.046	1.028

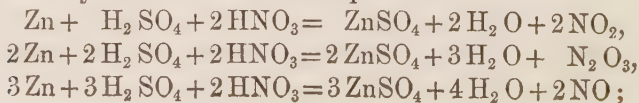
In these experiments the correction CR is only approximate, it being impossible to calculate the precise value of R with any great degree of accuracy; but evidently, except in the last one or two determinations, even a large error in the value of R would make no appreciable difference in the end result, viz. *that the E.M.F. of a Daniell cell regularly decreases as the current produced increases, but not at so rapid a rate.*

During the time that these observations were being made, the changes in the E.M.F. of the cell due to "running down" and variation of the density of the solutions surrounding the two plates respectively, were too small to be capable of measurement. After making an observation with

a larger current and reducing the current to a smaller value or to *nil*, sensibly the same value was always obtained whether at the beginning or end of the series of measurements, which lasted some two or three hours in each case. If, however, observations were made one day and then repeated a day or two after, concordance was rarely noticeable between the results: the later experiments always showed a more rapid rate of fall in the numerical value of $-e$ with the current-increase than the earlier ones, and also generally indicated a perceptibly lower value when the current was *nil*. Apparently this result was due to the deposition of copper on the surface of the zinc plate, owing to diffusion.

Experiments are now in progress in which the true value of R for any given cell is determined by a new method: so far these have given results entirely confirming those above described. The highest values hitherto obtained for the E.M.F. of a freshly arranged Daniell's cell generating an indefinitely minute current only, and freed from complicating circumstances as far as possible (especially presence of dissolved air, which tends slightly to lower the value), are between 1.105 and 1.110 volt (Clark's cell being 1.457 volt) at the temperature of 15° or thereabouts. The discussion of these experiments and of the valuations of the E.M.F. of a Daniell cell made by previous observers, and of the bearing on the discrepancies between these valuations of the point just substantiated (*viz.* the dependence of the E.M.F. on the current generated) will be resumed in a future paper. It may be noticed, however, that even with a not very enormous rate of current-flow per unit area, the diminution in E.M.F. amounts to several per cent. of the highest value, a quantity quite sufficient to vitiate observations in which the E.M.F. is assumed to remain constant.

98. Similarly the E.M.F. of a Grove's cell is not wholly independent of the current generated, although the effect is somewhat less marked than with a Daniell cell. The end result of the chemical changes taking place in this cell are expressed by one or other of the equations



so that, in addition to the production of gases (more or less completely absorbed by the nitric acid), dilution of the nitric acid takes place in the proximity of the platinum plate, thereby causing h' (the correction for the effects of differences in the density of the fluids surrounding the electrodes) to have an appreciable value. It is therefore to be expected that the E.M.F. of a Grove's cell will, like that of a Daniell's or an ordinary voltaic circle, decrease with the current generated. That this is actually the case is indicated by the following figures obtained with a "gravity" Grove's cell, the plates of which exposed an actual surface of 8 square centims. each, the calculated resistance of the column of fluid (partly concentrated nitric acid, partly 5-per-cent. sulphuric acid solution) between the plates being about 2 ohms, and the zinc plate being well amalgamated.

Current, in microwebers.	Microwebers per square centimetre.	E, in volts.	CR.	$-e = -(E - CR).$
0	0	-1.872	...	1.872
9.4	1.2	-1.872	...	1.872
18.7	2.3	-1.872	...	1.872
36.4	4.6	-1.872	...	1.872
93.6	11.7	-1.872	...	1.872
187.2	23.4	-1.872	...	1.872
466.2	58.3	-1.867	.001	1.768
930.5	116.3	-1.861	.002	1.863
1850.0	231.3	-1.850	.004	1.854
3678.0	459.8	-1.839	.007	1.846
8955.0	1119.4	-1.791	.018	1.809
17480.0	2185.0	-1.747	.035	1.782

99. It hence results that all methods for determining the E.M.F. of voltaic combinations, or for determining the internal resistance of cells, which depend on the production of currents of different magnitudes by means of the voltaic combination employed, may be erroneous to a considerable extent when it is assumed (as is ordinarily done) that the E.M.F. of the combination is independent of the current generated, and when the voltaic combination is such that this assumption is untrue, which is the case apparently in all the more common forms of cells, if indeed it is not universally the case. Thus, for instance, in Ohm's method for determining the E.M.F. of a cell, the current C_1 produced by the cell when connected with a galvanometer, the total resistance in circuit being R_1 , is determined ;

an additional resistance R_2 is then introduced, and the new current C_2 again determined. If the galvanometer be a sine-galvanometer, and α and β are the deflections in the two cases respectively,

$$C_1 = K \sin \alpha \text{ and } C_2 = K \sin \beta,$$

where K is a constant for the instrument. If the E.M.F. of the cell be supposed to be the same (E) for both currents, then

$$C_1 = K \sin \alpha = \frac{E}{R_1},$$

and

$$C_2 = K \sin \beta = \frac{E}{R_1 + R_2};$$

whence

$$\begin{aligned} E &= K \cdot R_2 \frac{\sin \alpha \cdot \sin \beta}{\sin \alpha - \sin \beta} \\ &= C_1 R_2 \frac{\sin \beta}{\sin \alpha - \sin \beta} \\ &= C_2 R_2 \frac{\sin \alpha}{\sin \alpha - \sin \beta}; \end{aligned}$$

that is, E is known in terms of the currents, the deflections, and the added resistance R_2 .

But if E be not the same for the two currents, being greater for the smaller by an amount δE , the equations become

$$C_1 = K \sin \alpha = \frac{E}{R_1},$$

and

$$C_2 = K \sin \beta = \frac{E + \delta E}{R_1 + R_2} = \frac{(1 + \delta)E}{R_1 + R_2};$$

whence

$$(1 + \delta)E = K \cdot \sin \alpha \cdot R_2 \frac{\sin \beta}{\sin \alpha - \frac{\sin \beta}{1 + \delta}}.$$

Evidently, if δ be assumed $=0$, the value of this expression is greater than the value when δ is not $=0$; that is, the assumption that the E.M.F. of the cell is constant throughout leads to the calculation of a value for its E.M.F. greater than the true value for the smaller current, and *à fortiori* greater than the true value for the larger current*.

* In H. F. Weber's experiments on the value of J (§ 55), a trifling source of error exists in those observations made with a voltaic battery,

In just the same way an incorrect value is obtained for the internal resistance of a cell by Ohm's method, which depends on the same principles. If R_1 be the resistance of the cell and R that of the rest of the circuit, a current is generated

$$C_1 = K \sin \alpha = \frac{E}{R + R_1},$$

and by throwing in an extra resistance R_2 the current is reduced to

$$C_2 = K \sin \beta = \frac{E(1 + \delta)}{R + R_1 + R}.$$

If it be assumed that $\delta = 0$, then

$$R_1 = R_2 \frac{\sin \beta}{\sin \alpha - \sin \beta} - R;$$

but if δ is not equal to 0, then

$$R_1 = R_2 \frac{\sin \beta}{(1 + \delta) \sin \alpha - \sin \beta} - R,$$

which is manifestly less than the former value; so that the assumption that the E.M.F. of the cell is constant throughout leads to the overvaluation of its internal resistance.

100. The results above described have an important bearing on a considerable amount of work performed by Favre (*Comptes Rendus*, 1866 and following years). By passing a current through an electrolytic cell placed in a calorimeter, an external resistance being in circuit so large that the resistance of the cell was wholly negligible (?) in comparison with it, and consequently the heat developed in accordance with Joule's law was practically *nil*, Favre obtained values in terms of heat corresponding to the difference between the work done in decomposing the electrolyte into the primary and the final products of decomposition. *E. g.* in one set of experiments with water, the actual mean heat-development was close to 14,000 gramme-degrees per gramme-

the mean E.M.F. of which during the experiment was measured as a necessary part of the data; for the measurement gives the E.M.F. corresponding to a current C_1 , whilst the heat evolved was that caused by a different current C_2 . As, however, Weber states that C_1 was always approximately $= C_2$, this source of error is not great and is probably negligible, since the B.A. resistance values got by this method are sensibly the same as those obtained by the two other independent methods employed.

equivalent of water decomposed; adding to this 34,100 gramme-degrees, the heat corresponding to the formation of gaseous oxygen and hydrogen (Part I. § 31), it results that in this experiment the total work done during the electrolysis was equivalent to 48,100 gramme-degrees, or 2.12 volts; *i. e.* the mean value of e in these experiments was 2.12 volts. By comparing together various values obtained in this way with different electrolytes, Favre was led to the conclusion that of this 14,000 gramme-degrees (which he regarded as a constant heat-absorption during water-electrolysis over and above the heat taken up in the formation of gaseous oxygen and hydrogen = 34,100), about 9500 were due to the transformation of allotropic oxygen formed by the first action of the current into ordinary oxygen gas, and the remainder to the transformation of allotropic hydrogen into ordinary hydrogen gas. The above-described results, however, indicate that these particular numerical values have only reference to the particular apparatus and current-strengths used by Favre: had the size of the electrodes been varied, or their nature, or the current-strength, quite different numbers would have been obtained in each case, not only in these particular experiments cited, but also in a number of other analogous ones with other substances; for each change would have brought about a corresponding change in the value of e , and hence in the heat-evolution. Apart from this, however, as Favre's values were obtained with the mercury-calorimeter, a considerable probable error attends the determinations; so that finally no reliance at all can be placed on the conclusions arrived at by Favre in this series of experiments, as regards numerical values.

It is noticeable in this connexion, that experiments by Raoult (*Annales de Chimie et de Phys.* ii. p. 317, and iv. p. 392, 1864 and 1865) show that the value of the counter electromotive force set up during electrolysis varies with the current *ceteris paribus*. Raoult observed the "subsequent polarization" of an electrolytic cell very quickly after the rupture of the current, determining it in terms of a Daniell's cell, this being itself valued in terms of the heat producible by its current whilst a gramme-equivalent of copper was precipitated. The difference between the heat actually evolved in

the cell (measured by a calorimeter) and that equivalent to the polarization, was termed by Raoult "Local Heat," and found by him to be larger with stronger currents. The results above described with a Daniell cell, however, show that the valuation in terms of heat of a Daniell cell is not a constant quantity; for the heat capable of being evolved by the current outside the battery during the precipitation of a gramme-equivalent of copper, being proportional to the E.M.F. of the cell, is variable with the time during which this precipitation takes place, *i. e.* with the strength of the current; whilst the "subsequent polarization," measured by Raoult, being always more or less inferior to the counter E.M.F. set up during the passage of the current, is not the true measure of the electrolytic work done by the current whilst it was passing through the cell.

Notwithstanding, however, that the numerical results of Favre and Raoult are open to exception, these observers were amongst the first, if not actually the first, to attempt to carry out experimentally some of the lines of research opened out by Sir W. Thomson (1851 paper), although the theoretical aspects of the question, as discussed by them, do not entirely coincide with Thomson's mode of reasoning.

Summary of Results.

101. The following summary briefly indicates the salient results arrived at in Parts III. and IV. of these researches.

(1) The passage of a given quantity of electricity through an electrolyte causes the decomposition of one and the same amount of substance, irrespective of the time taken in its passage; in other words, conduction without electrolysis does not take place, and Faraday's law is true for excessively minute currents as well as for those of considerable magnitude.

(2) With very feeble currents, however, and with certain electrolytes, *e. g.* water, the quantity of products of decomposition actually collected after a given time, does not absolutely correspond to the quantity of electricity that has passed, even after various sources of suppression have been eliminated, such as occlusion in or condensation on the electrodes, solution in the fluid, or suppression by the chemical action of dissolved gases. The cause of this is the "diffusion discharge"

produced (in the case of water) by the diffusion towards the — electrode of water containing dissolved oxygen, and towards the + electrode of fluid containing dissolved hydrogen (and similarly in other cases), thus causing an unavoidable suppression by chemical action. When the amount of suppression due to this cause is determined and added to the observed amount of decomposition, the total corresponds exactly with the quantity of electricity that has passed.

(3) In the electrolysis of acidulated water, until the sources of loss of hydrogen other than “diffusion discharge” are eliminated (viz. solution in the fluid, condensation and absorption by the electrode, and action of dissolved oxygen originally present in the fluid), the counter E.M.F. set up when a given steady current traverses a given voltmeter is short of its maximum value for that current; simultaneously a deficiency in the amount of hydrogen collected as compared with that due to the quantity of electricity passing is noticed (even after correction for diffusion discharge); whilst on breaking circuit, the rate of fall of the “polarization” of the electrodes is more rapid than its minimum value for that current. On the other hand, as soon as the counter E.M.F. reaches its maximum, the deficiency in hydrogen disappears (after correction for diffusion discharge), and the rate of fall of the polarization after breaking circuit reaches its minimum. The more nearly completely the sources of loss are eliminated, the more nearly does the counter E.M.F. set up approach its maximum, the less is the deficiency in the hydrogen collected, and the more nearly does the rate in fall of polarization approach its minimum.

(4) A theory has been enunciated, and more or less completely demonstrated, which reconciles the hitherto apparently contradictory numerical values obtained by previous observers for the counter E.M.F. set up during electrolysis, the “subsequent polarization” existing after rupture of the current, and the E.M.F. of gas batteries. In accordance with this theory, the relationships between the current flowing and the counter E.M.F. set up in an electrolytic cell are expressed by the following formula:—

$$e = E + [\Sigma\{(1-n)H\} - \Sigma(nh) - \Sigma(H)]\chi J.$$

(5) In the case of all the electrolytes examined, the value

of e is found to increase as the current increases, but at a less rapid rate, so that the curves traced out by plotting currents as abscissæ and counter E.M.F. values as ordinates are concave downwards.

So long as the rate of flow per unit area of electrode surface remains the same, the value of e is constant; *i. e.* if the electrode surface and the current vary in the same way, then e remains the same. With a given current increasing the electrode surface diminishes the value of e .

The values of e depend on the material of which the electrodes are made. Other things being equal, carbon gives higher values than platinum, and platinum than gold.

In the case of acidulated water, rendering the solution more dilute increases the value of e .

From former observers' work it results that increasing the temperature decreases e .

(6) The above formula, in conjunction with experimental determinations of the variations in the values of e under various conditions, explains coherently and quantitatively the leading facts connected with counter E.M.F., polarization, and the E.M.F. of gas-batteries, and accounts for the possibility, under certain conditions, of decomposing an electrolyte with a less battery E.M.F. than corresponds to the work done in splitting it up into the final products—and also indicates that the E.M.F. of a Daniell cell is not constant, but is less the greater the current it generates, to such an extent that with currents of not very great magnitude a diminution in E.M.F. to the extent of several per cent. is brought about, and that, in consequence, certain of the methods in use for determining the E.M.F. of cells and their internal resistance are, at any rate for certain kinds of cells, incorrect, as they are based on the assumption that the E.M.F. of the cell is constant.

(7) By means of the above formula and the experimental determinations of the causes which make e to vary, &c., information can be deduced as to the amount of energy with which gases are condensed upon the surface of solids, and in particular as to the amount of energy requisite to break up an electrolyte into "nascent" products solely. By conjoining this determination with the determination of the methods for finding the E.M.F. corresponding to the energy requisite to

break it up into the final products (described in Parts I. and II.), information can be deduced concerning the affinity of the constituents of the electrolyte, and the variations of that affinity according as the constituents are "nascent" or in their ordinary free state. For instance, the energy given out in the transformation of nascent hydrogen and oxygen into the ordinary free gases exceeds the energy that would be developed by the union of these gases to form liquid water, *i. e.* exceeds the energy equivalent to 34100 gramme-degrees or to 1.50 volt.